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Alvarez, Jr. et al.

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(45) **Date of Patent: Jul. 5, 2005**

(54) **METHOD FOR THE REMOVAL OF AIRBORNE MOLECULAR CONTAMINANTS USING WATER GAS MIXTURES**

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(22) Filed: **Oct. 10, 2003**

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Related U.S. Application Data

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(51) **Int. Cl.**[7] **B08B 5/00**

(52) **U.S. Cl.** **134/11**; 134/2; 134/10; 134/22.1; 134/21; 134/22.11; 134/26; 134/31; 134/34; 134/36; 134/37; 134/42

(58) **Field of Search** 134/2, 10, 11, 134/21, 22.1, 22.11, 26, 31, 34, 36, 37, 42

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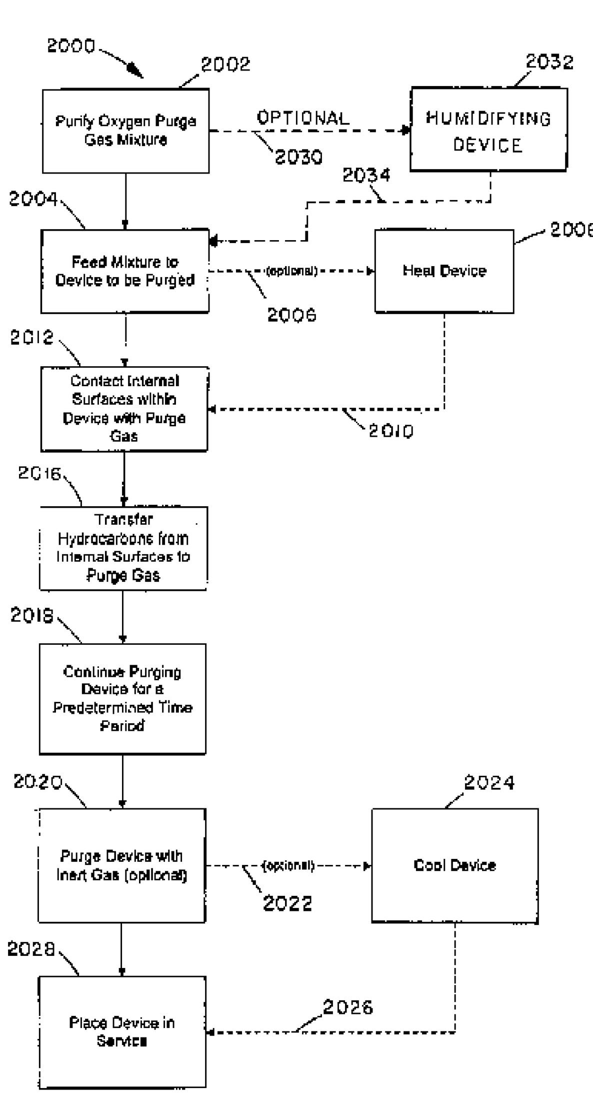
Primary Examiner—S. Carrillo
(74) *Attorney, Agent, or Firm*—Hamilton, Brooks, Smith & Reynolds, P.C.

(57) **ABSTRACT**

The present invention discloses a method for the removal of a number of molecular contaminants from surfaces within a device. A purge gas containing oxygen and/or water is introduced into the interior of the device, contacting at least a portion of the interior surfaces. A contaminated purge gas is produced by transferring a portion of the contamination from the interior surfaces into the purge gas. The contaminated purge gas is removed from the device and the process is continued until the contaminant concentration in the contaminated purge gas is below a predetermined level.

11 Claims, 19 Drawing Sheets



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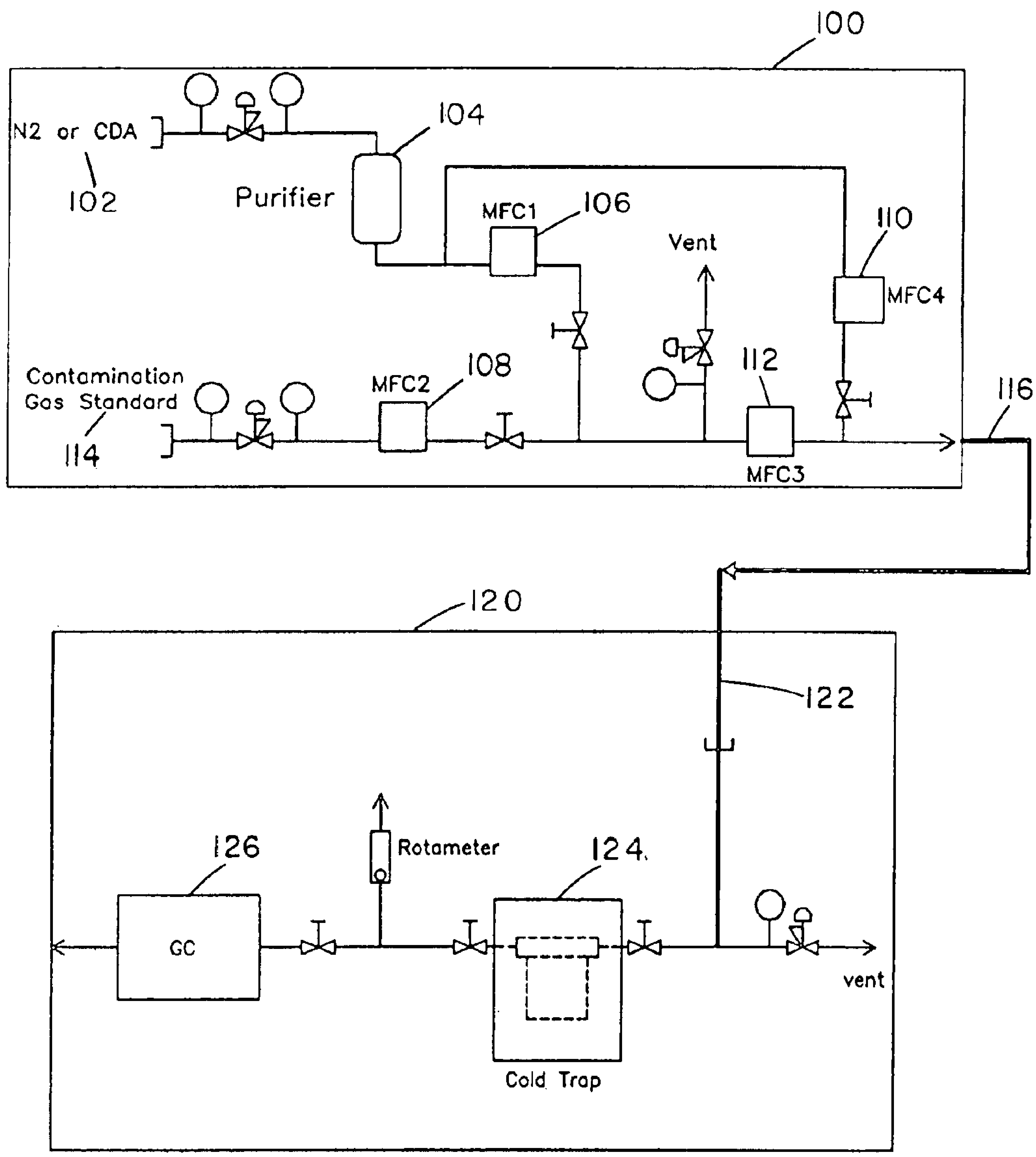


FIG. 1 PRIOR ART

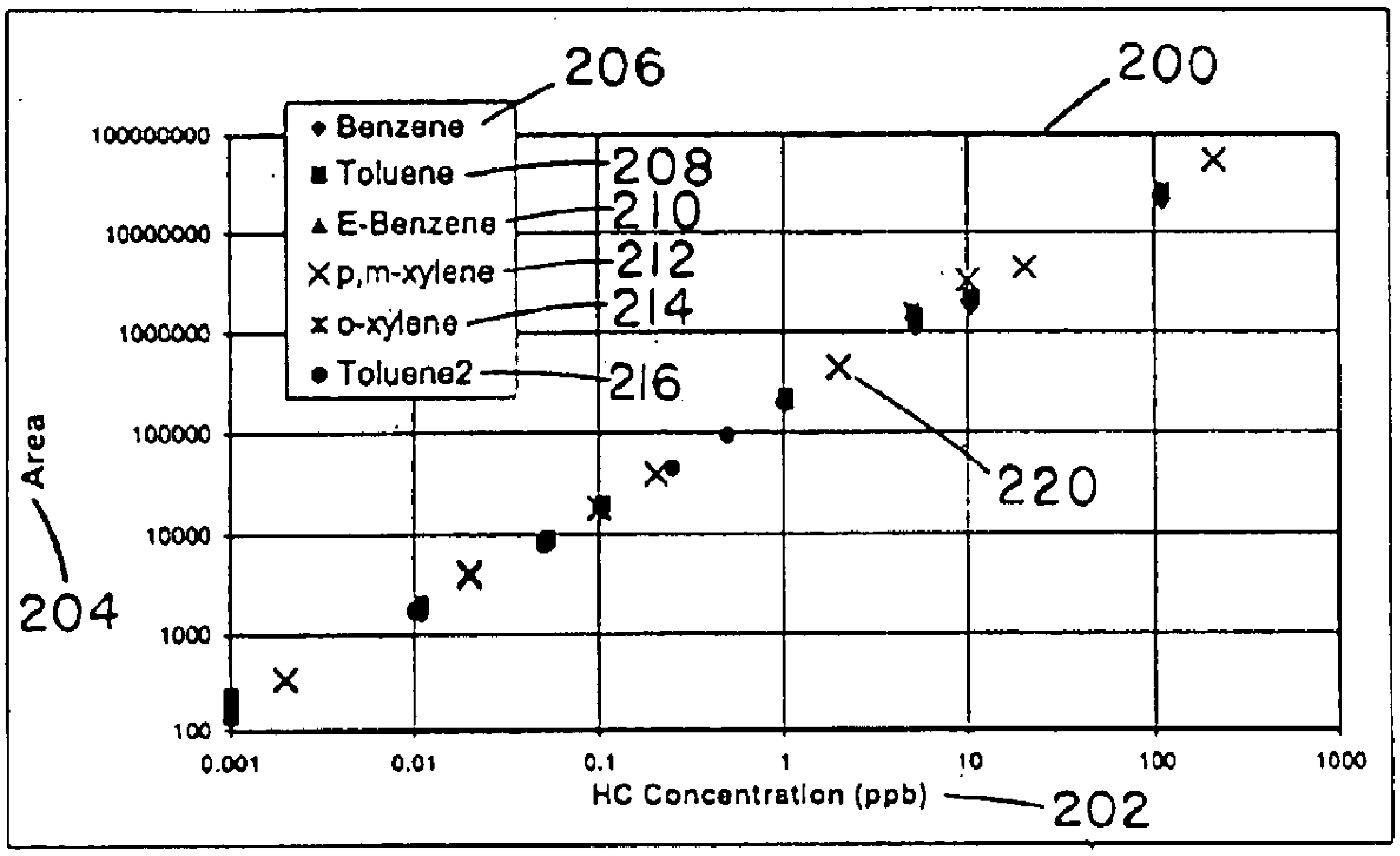


FIG. 2 PRIOR ART

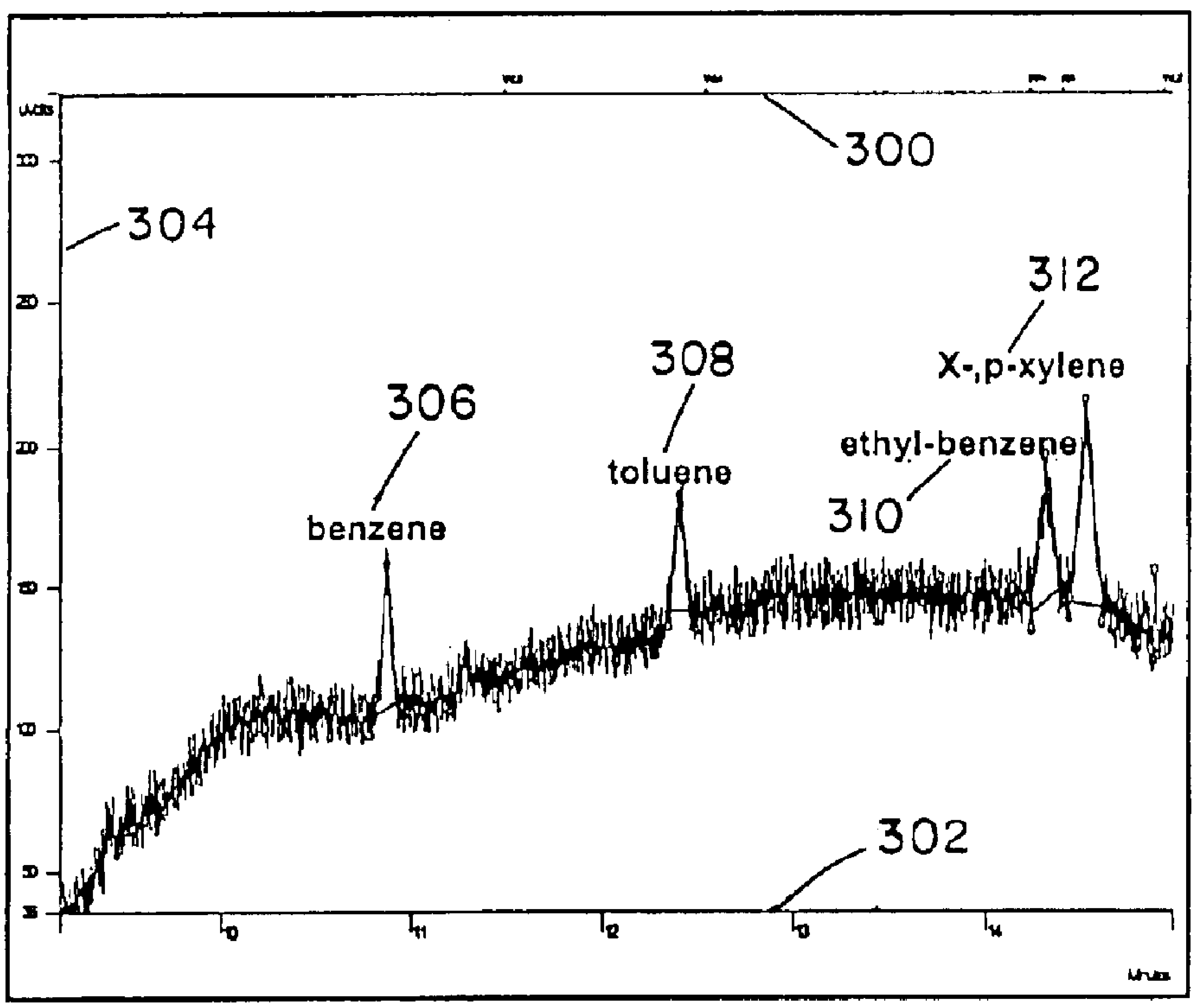


FIG. 3 PRIOR ART

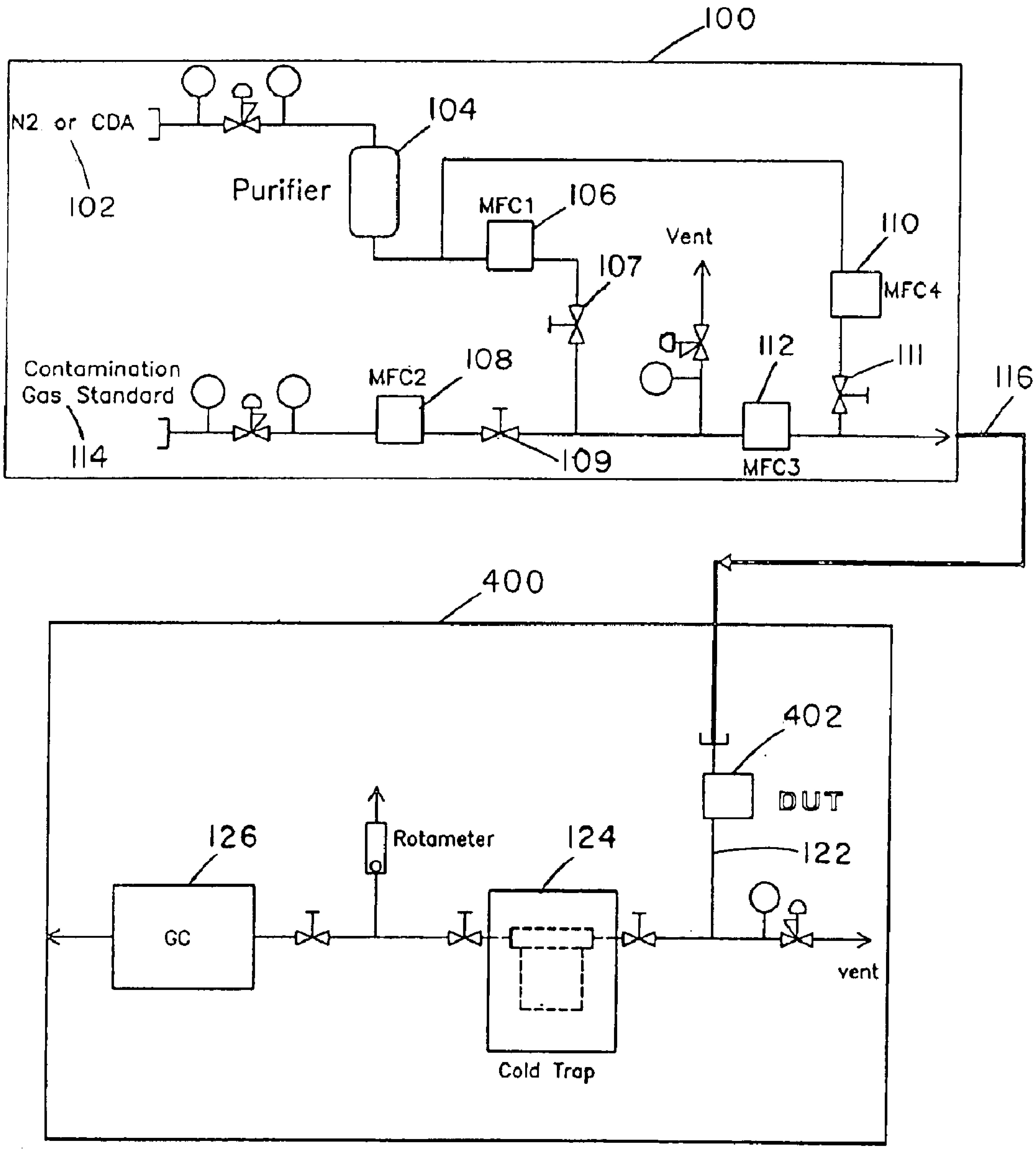
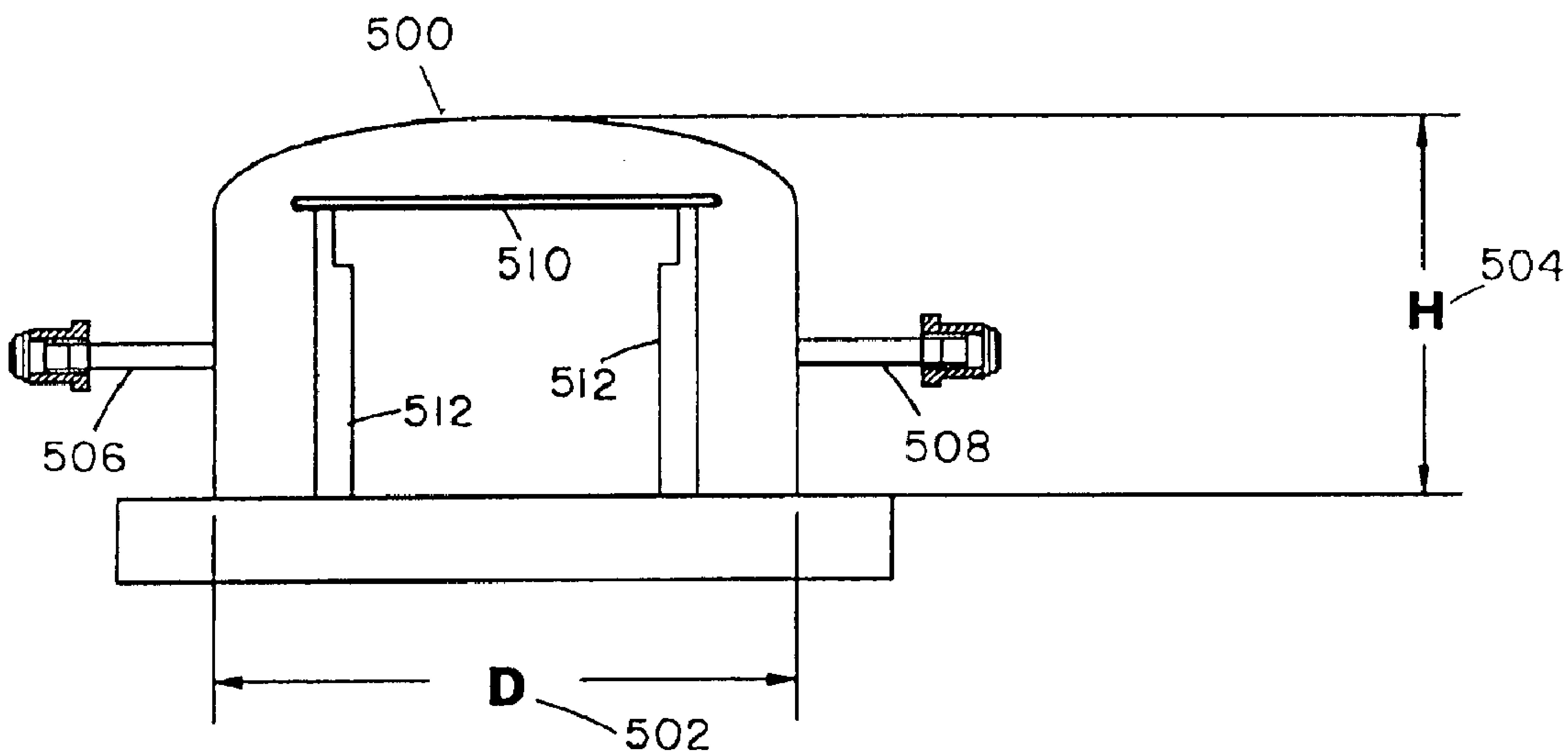

100
N2 or CDA
102
Purifier
104
MFC1
106
Vent
107
110
MFC4
Contamination Gas Standard
114
MFC2
108
109
112
MFC3
111
116
400
402
DUT
122
126
Rotameter
124
GC
Cold Trap
vent

FIG. 4



Wafer Chamber

FIG. 5

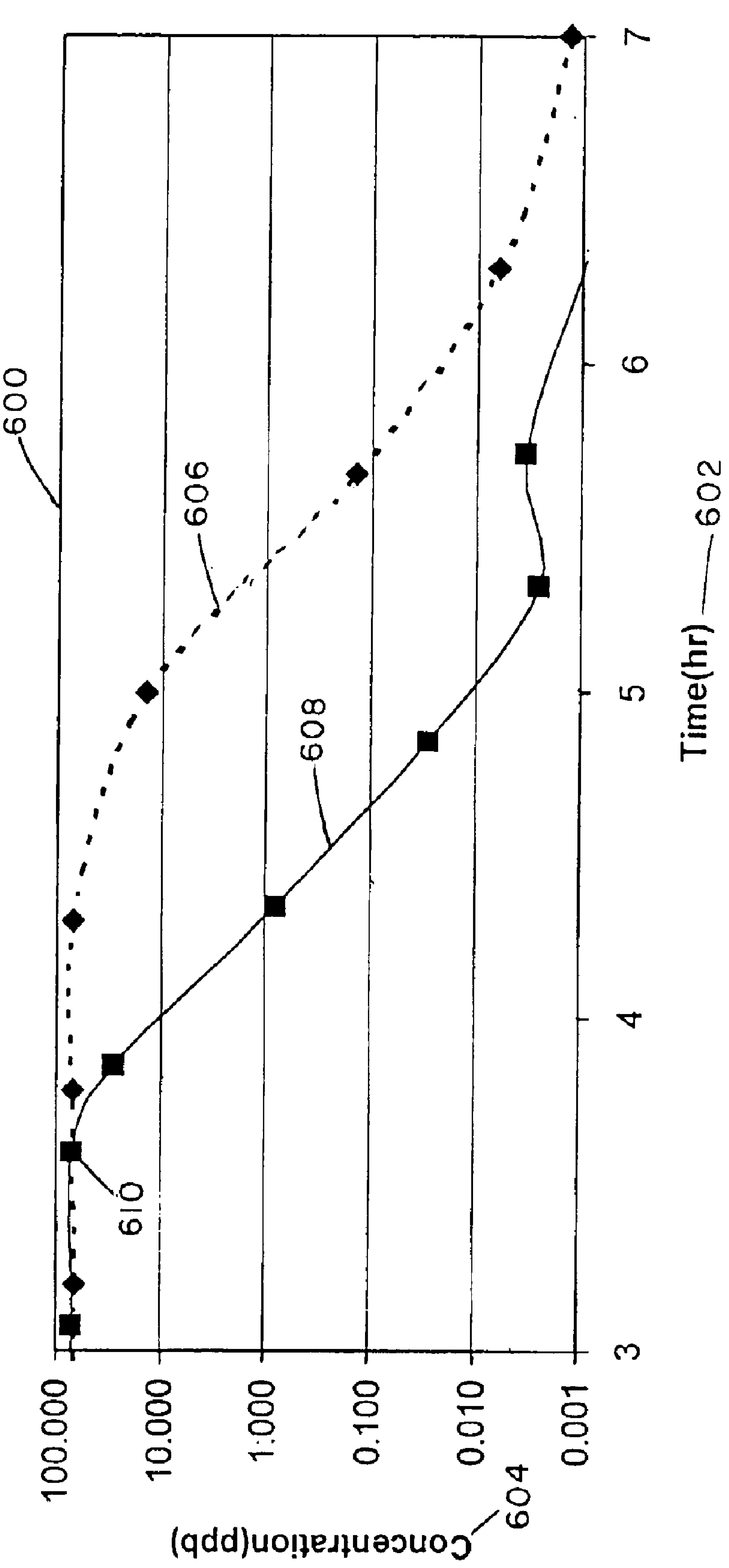

600
606
608
610
602
604
Time(hr)
Concentration(ppb)
3
4
5
6
7
100.000
10.000
1.000
0.100
0.010
0.001

FIG. 6

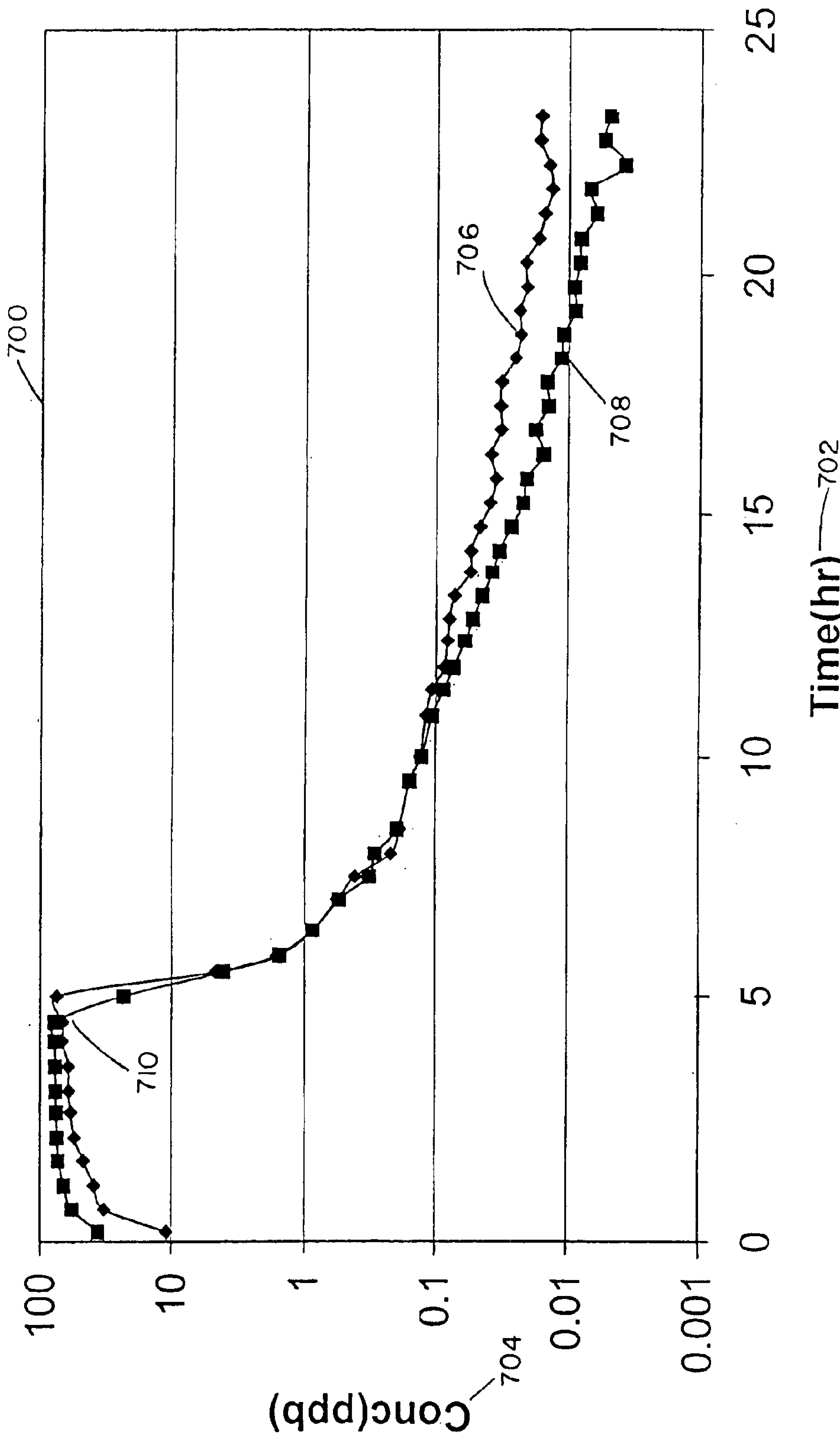

700
100
10
1
0.1
0.01
0.001
Conc(ppb)
704
0
5
10
15
20
25
Time(hr)
702
706
708
710

FIG. 7

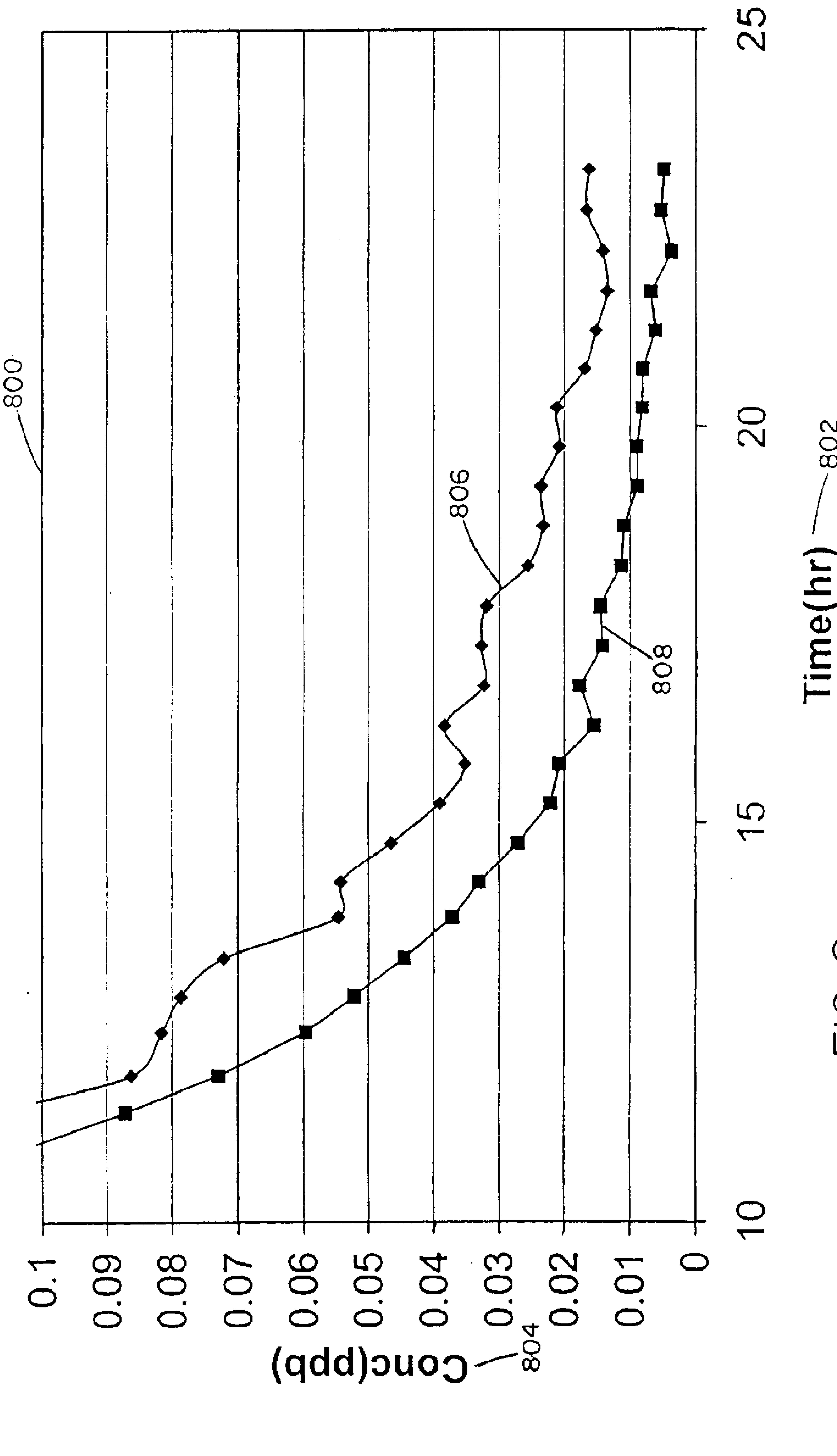

800
Conc(ppb)
804
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
10
15
20
25
Time(hr)
802
806
808

FIG. 8

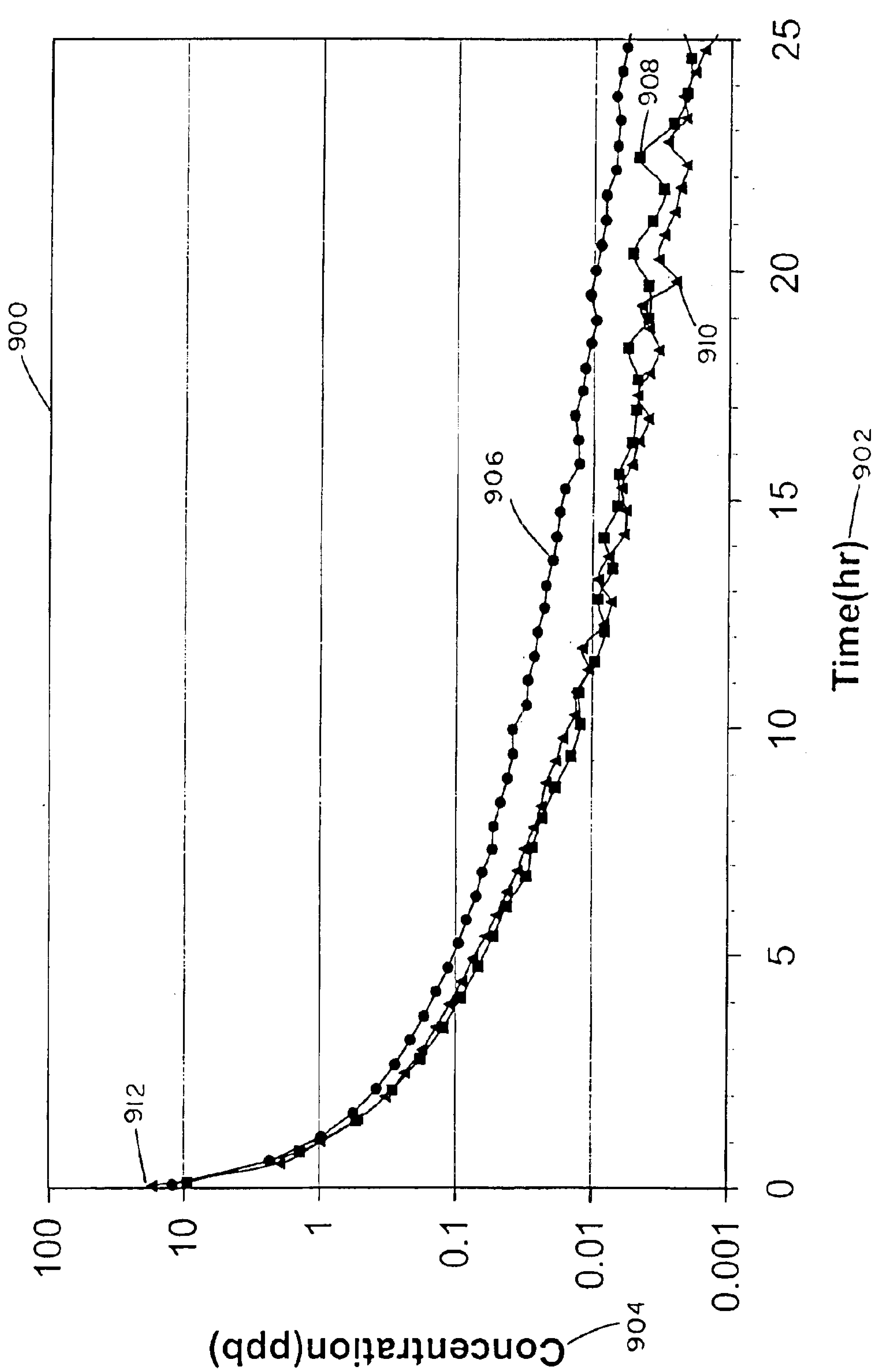
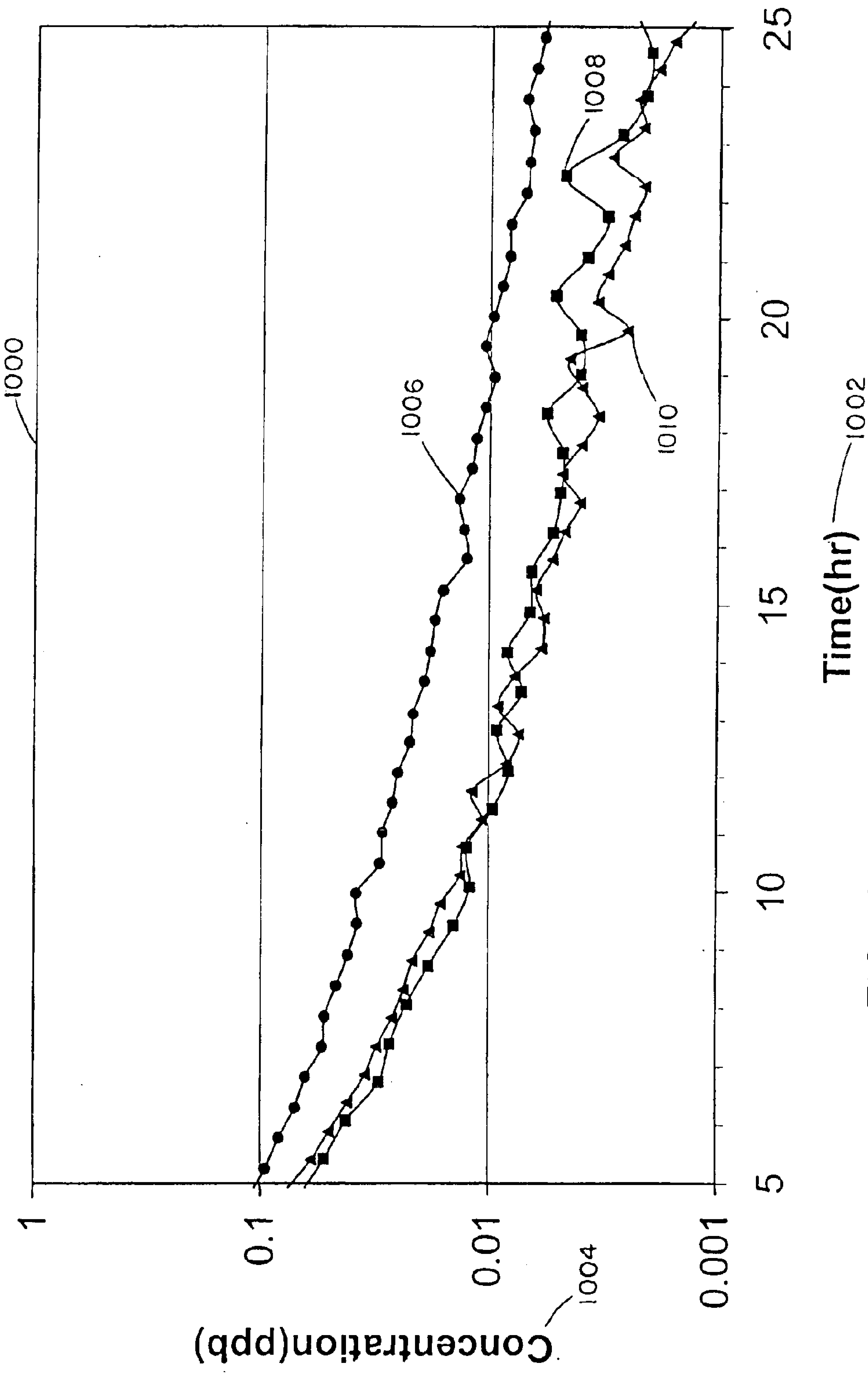

900
Concentration(ppb)
904
100
10
1
0.1
0.01
0.001
Time(hr)
902
0
5
10
15
20
25
906
908
910
912

FIG. 9



1000
1002
1004
1006
1008
1010
Time(hr)
Concentration(ppb)
1
0.1
0.01
0.001
5
10
15
20
25

FIG. 10

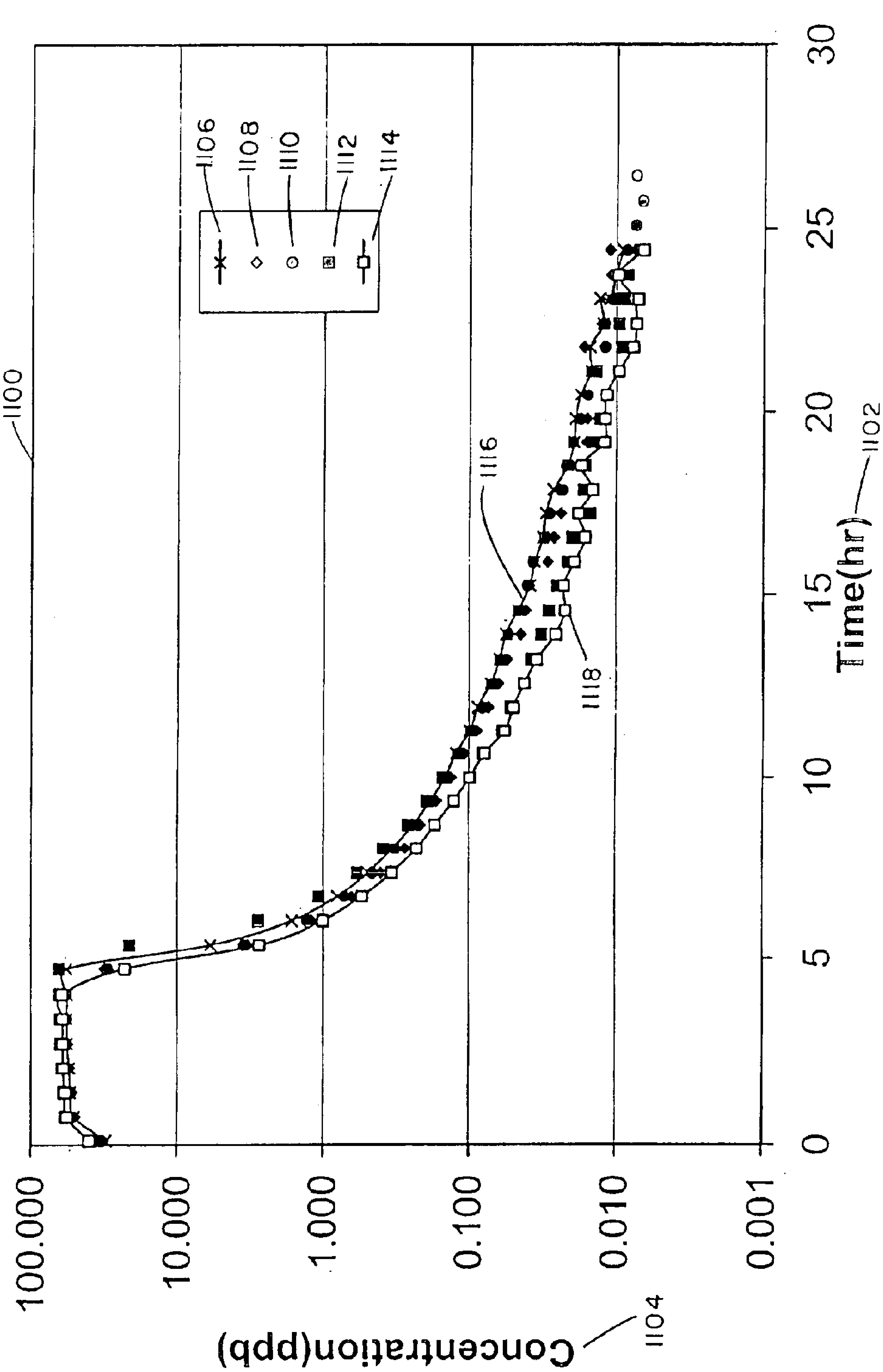

1100
1102
1104
1106
1108
1110
1112
1114
1116
1118
Concentration(ppb)
Time(hr)
100.000
10.000
1.000
0.100
0.010
0.001
0
5
10
15
20
25
30

FIG. 11

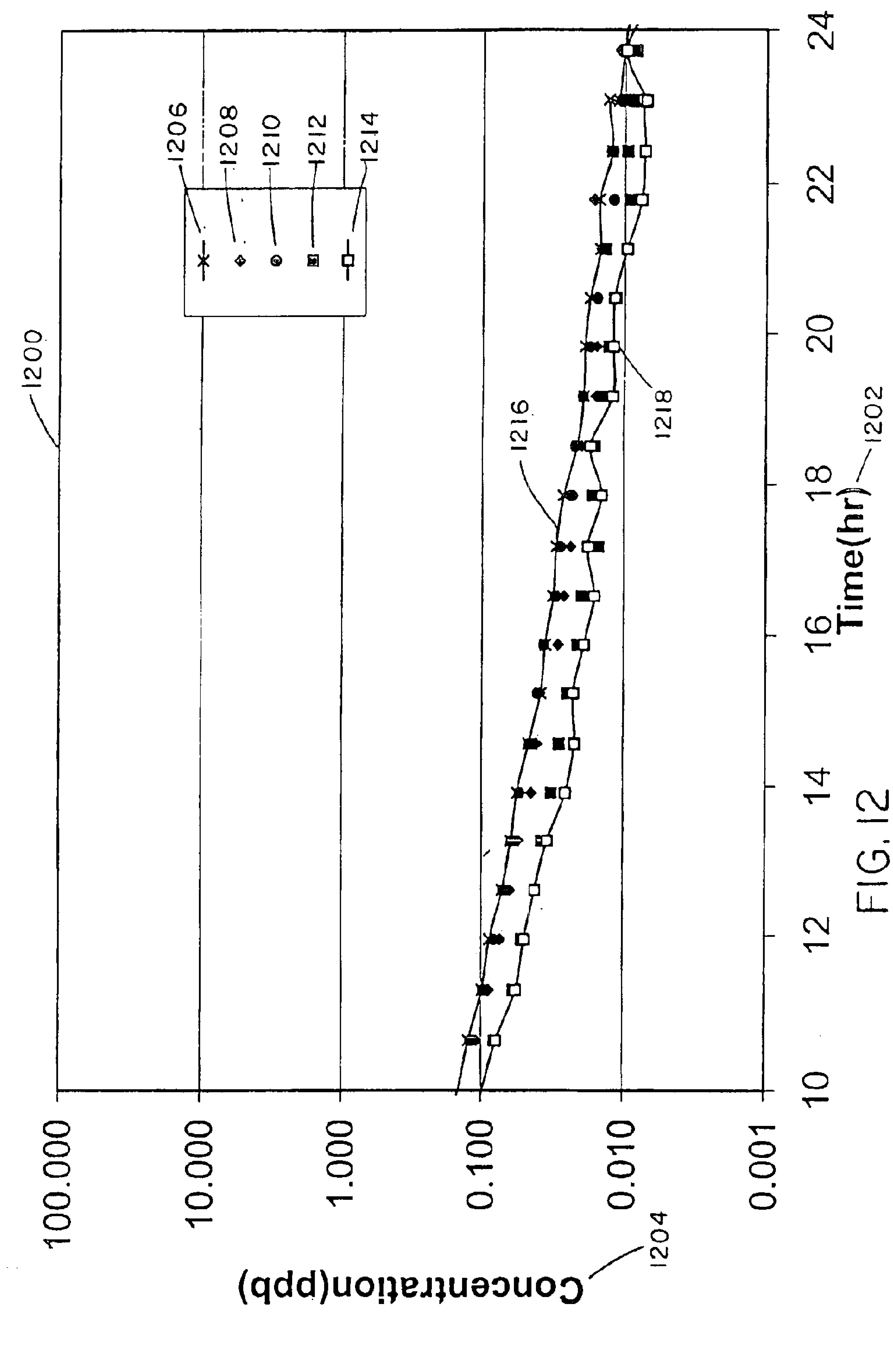

1200
1202
1204
1206
1208
1210
1212
1214
1216
1218
Concentration(ppb)
100.000
10.000
1.000
0.100
0.010
0.001
Time(hr)
10
12
14
16
18
20
22
24

FIG. 12

Figure 13

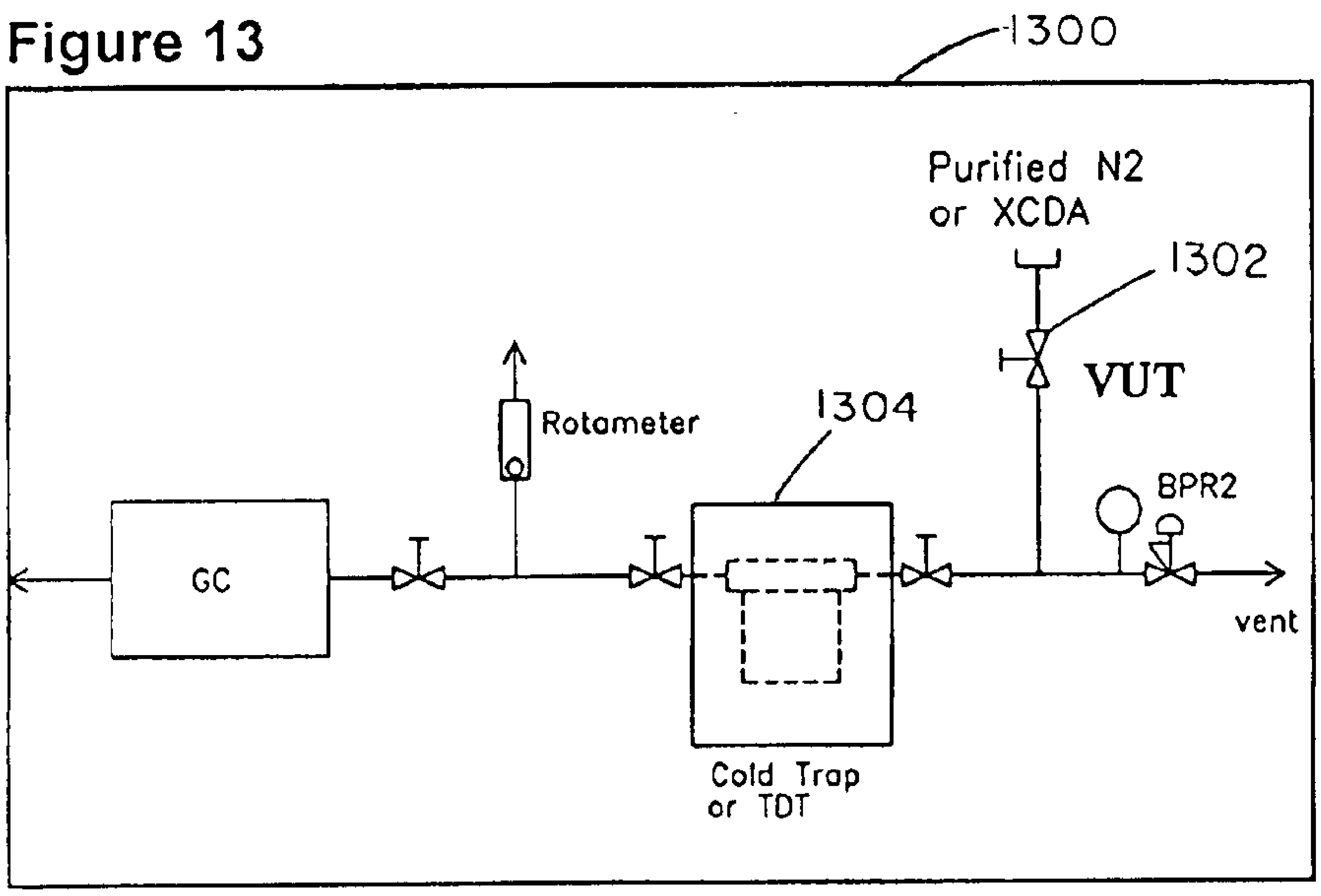


Figure 14

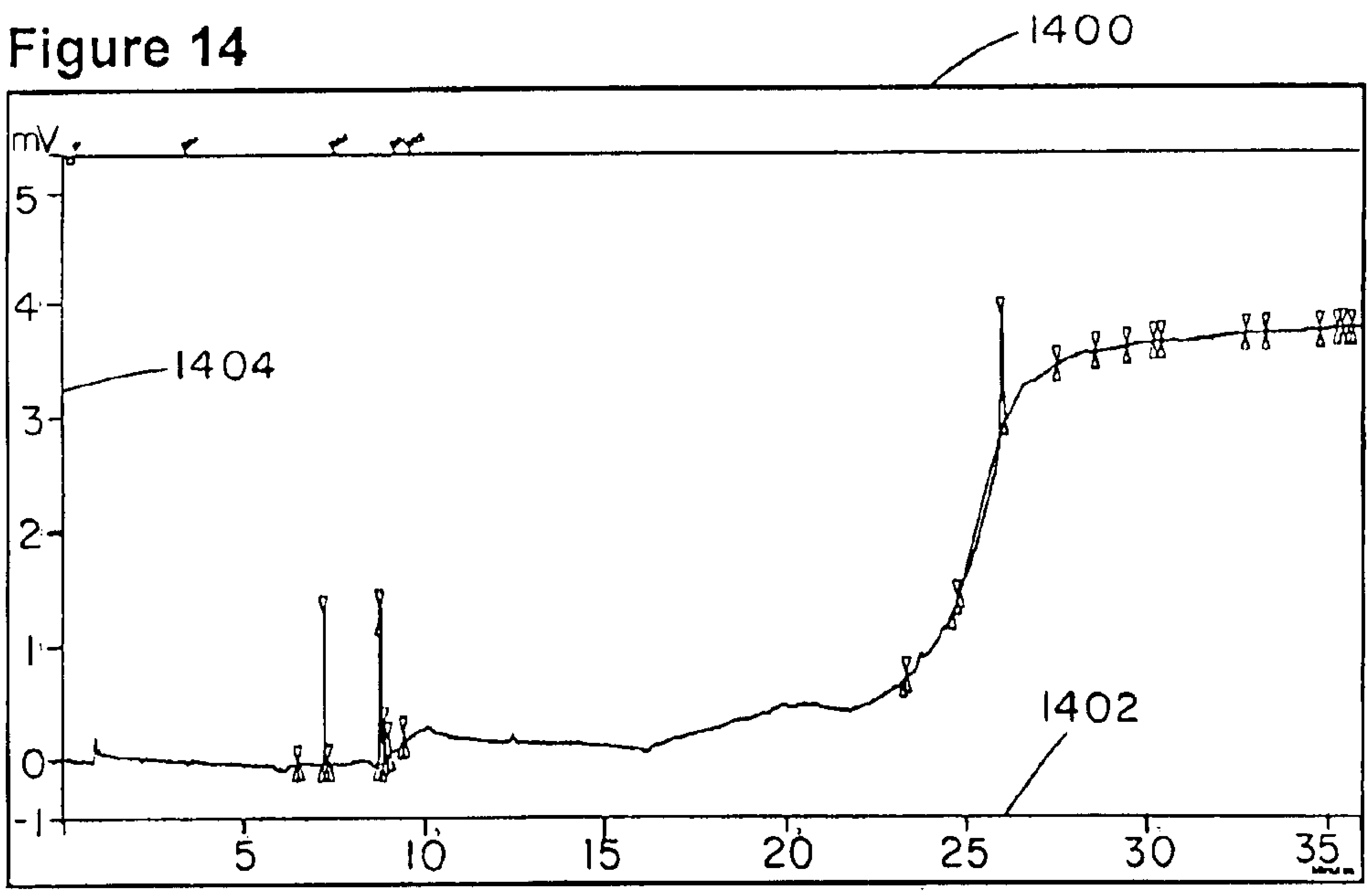
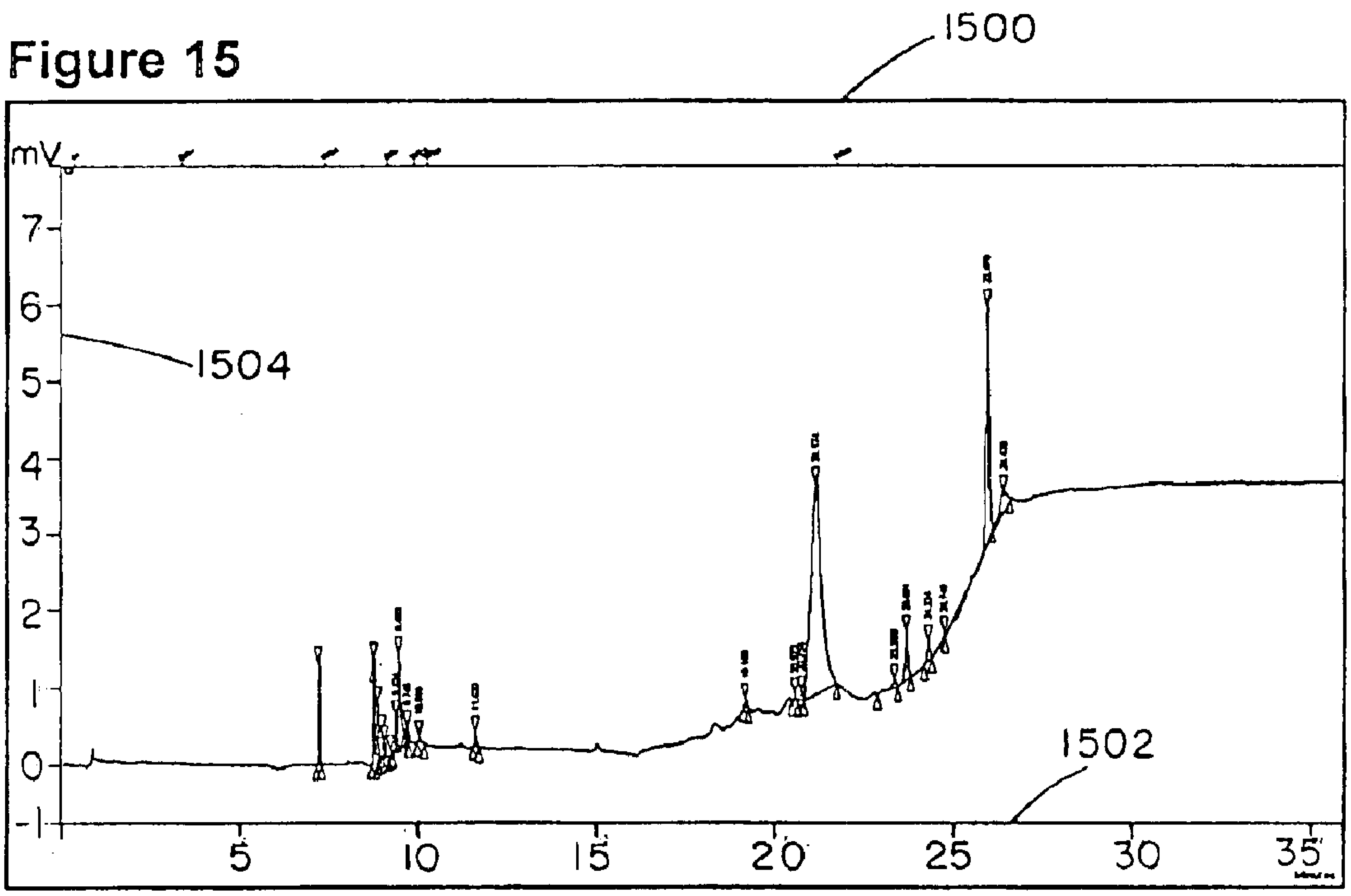


Figure 15



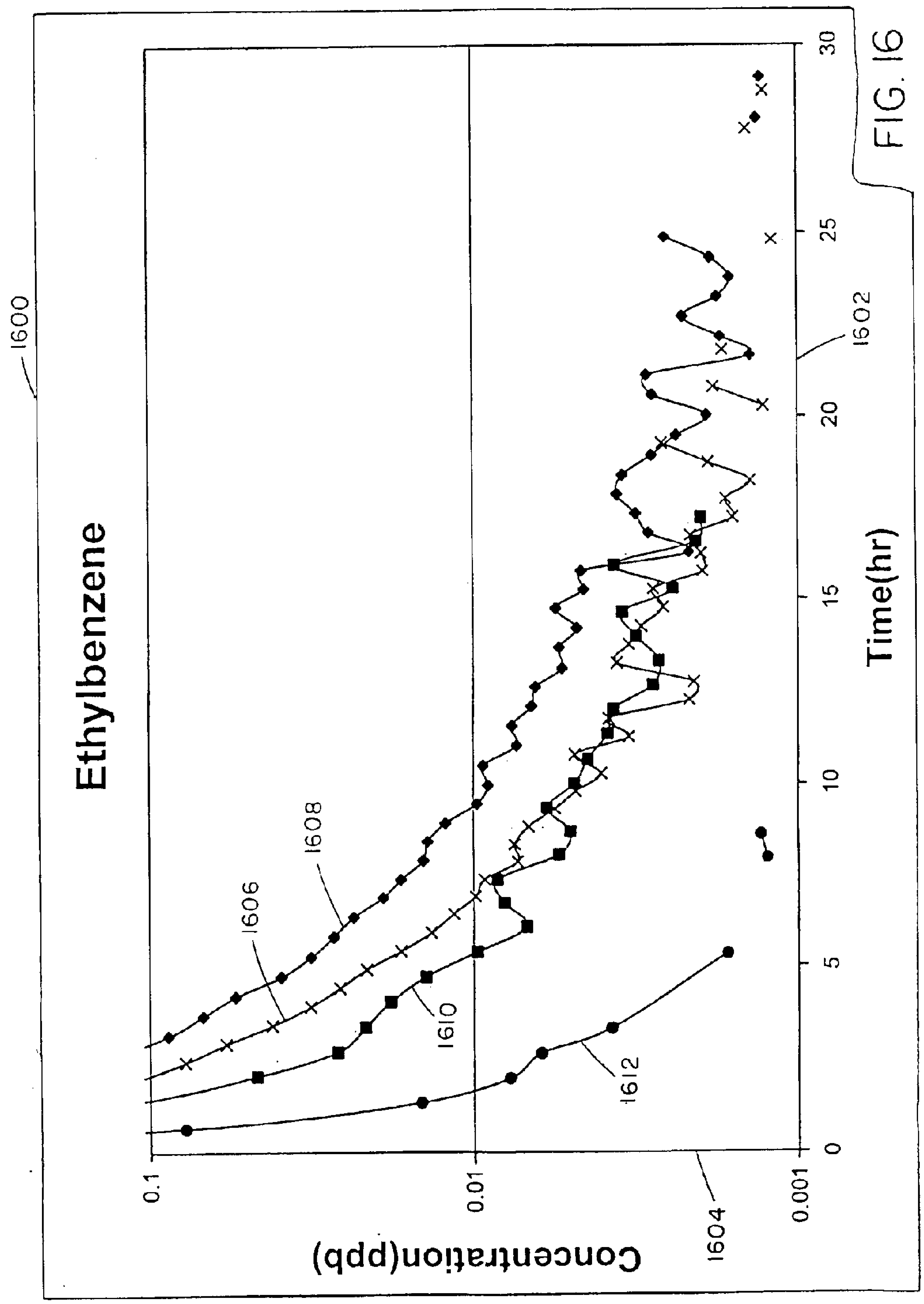

1600
Ethylbenzene
Concentration(ppb)
0.1
0.01
0.001
Time(hr)
0
5
10
15
20
25
30
1602
1604
1606
1608
1610
1612

FIG. 16

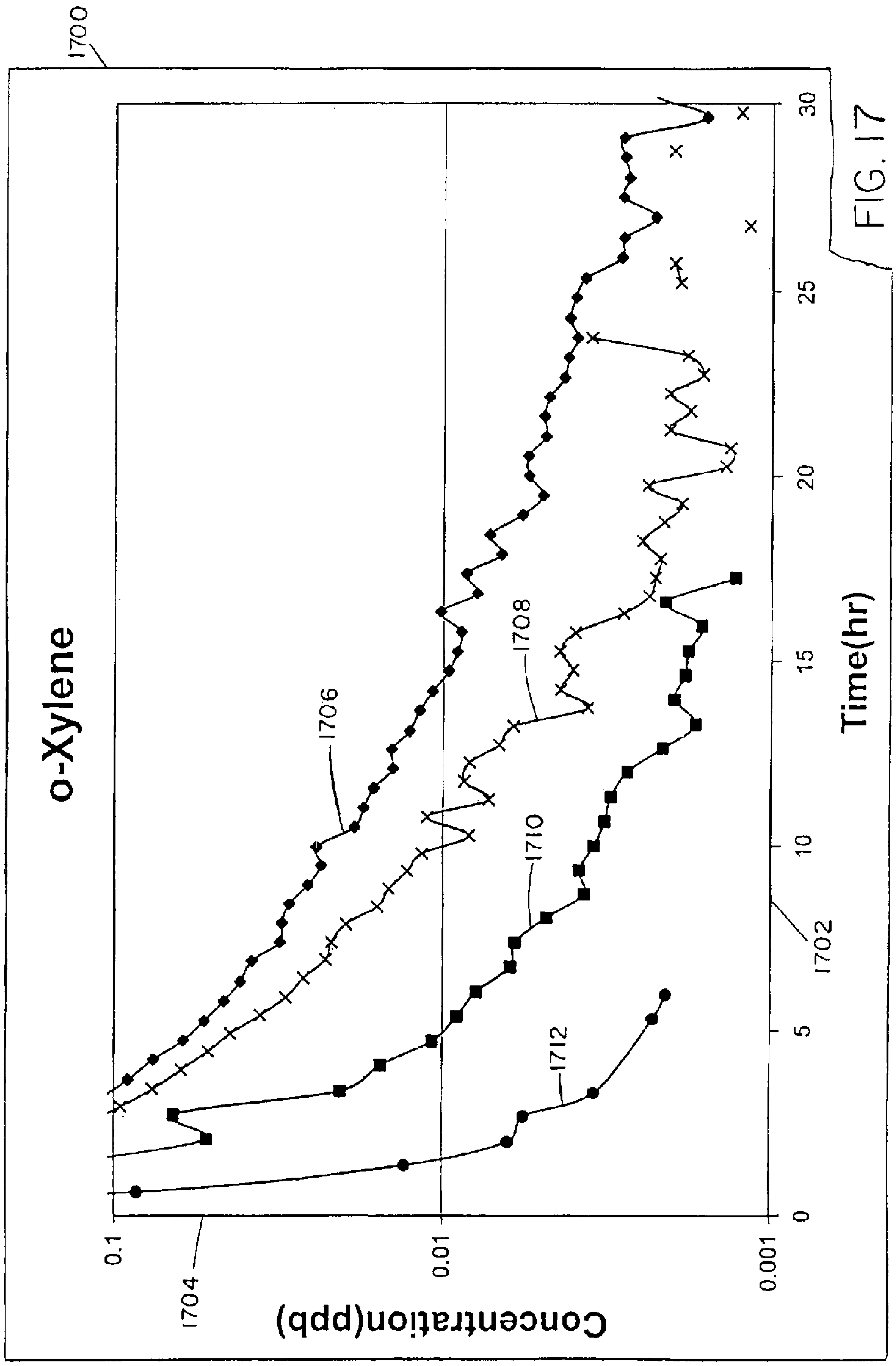

1700
o-Xylene
Concentration(ppb)
Time(hr)
0.1
0.01
0.001
0
5
10
15
20
25
30
1702
1704
1706
1708
1710
1712

FIG. 17

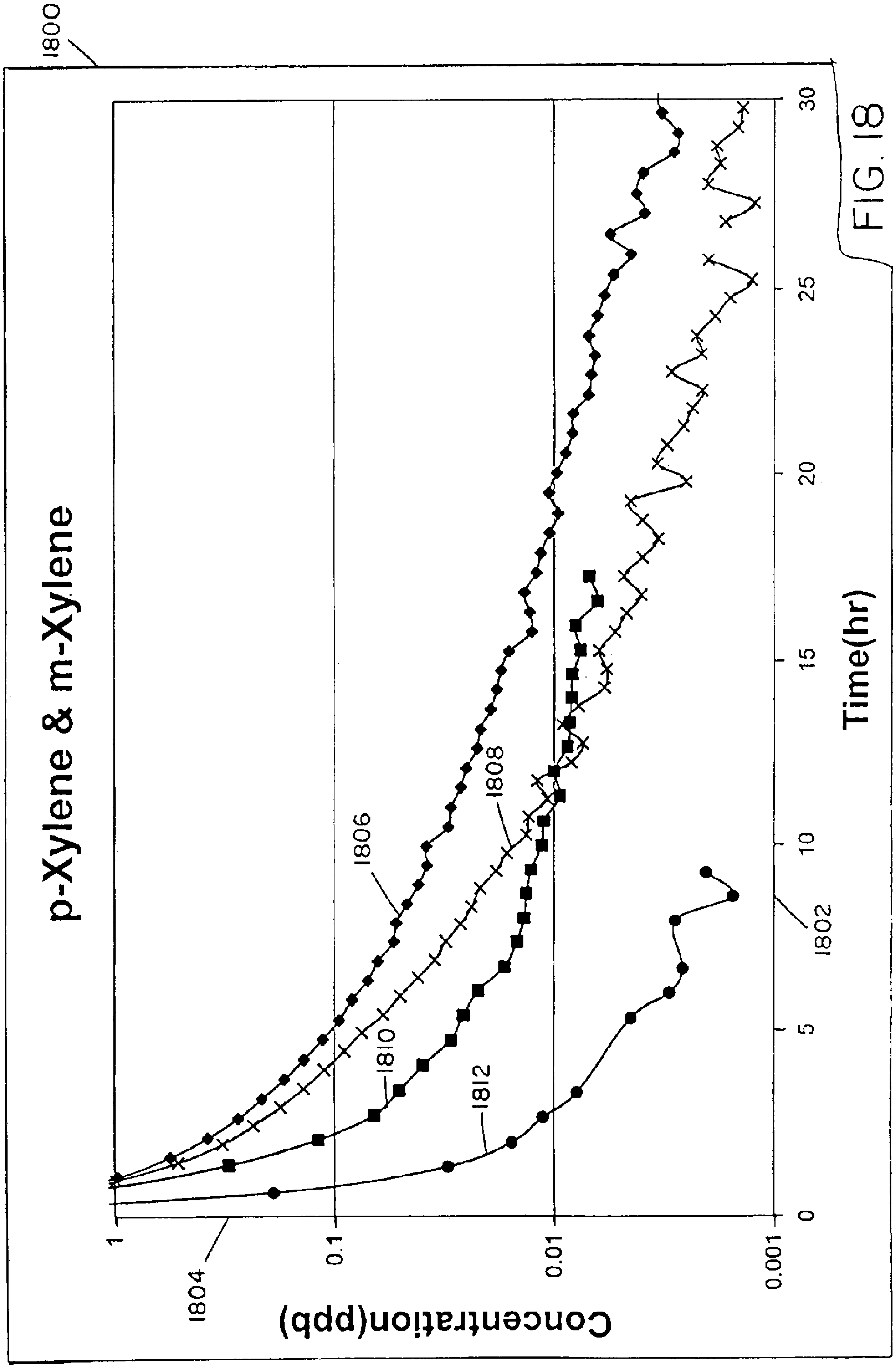

1800
p-Xylene & m-Xylene
Concentration(ppb)
1
0.1
0.01
0.001
Time(hr)
0
5
10
15
20
25
30
1802
1804
1806
1808
1810
1812

FIG. 18

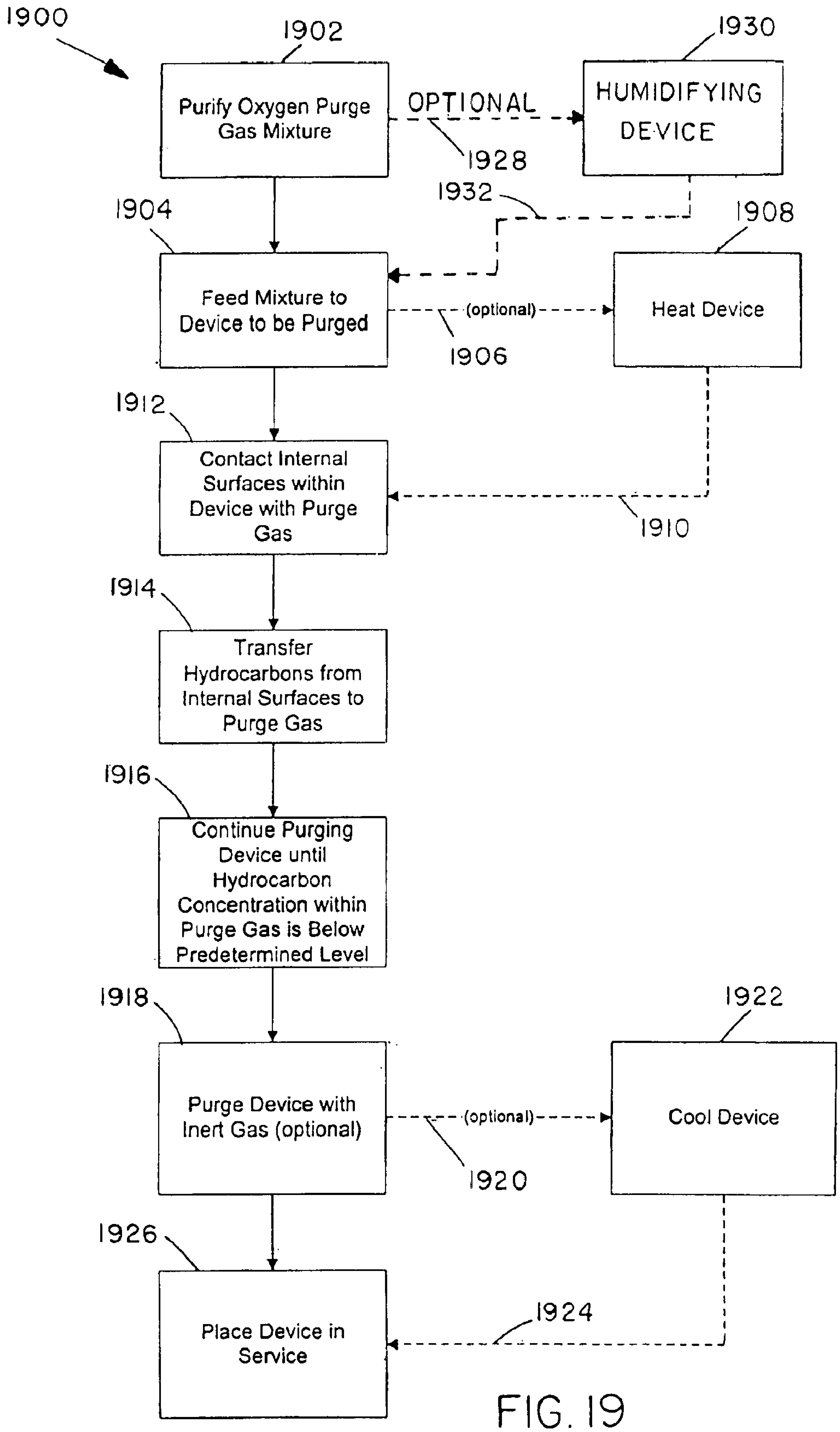

1900
1902
Purify Oxygen Purge Gas Mixture
OPTIONAL
1928
1930
HUMIDIFYING DEVICE
1932
1904
Feed Mixture to Device to be Purged
(optional)
1906
1908
Heat Device
1912
Contact Internal Surfaces within Device with Purge Gas
1910
1914
Transfer Hydrocarbons from Internal Surfaces to Purge Gas
1916
Continue Purging Device until Hydrocarbon Concentration within Purge Gas is Below Predetermined Level
1918
Purge Device with Inert Gas (optional)
(optional)
1920
1922
Cool Device
1926
Place Device in Service
1924

FIG. 19

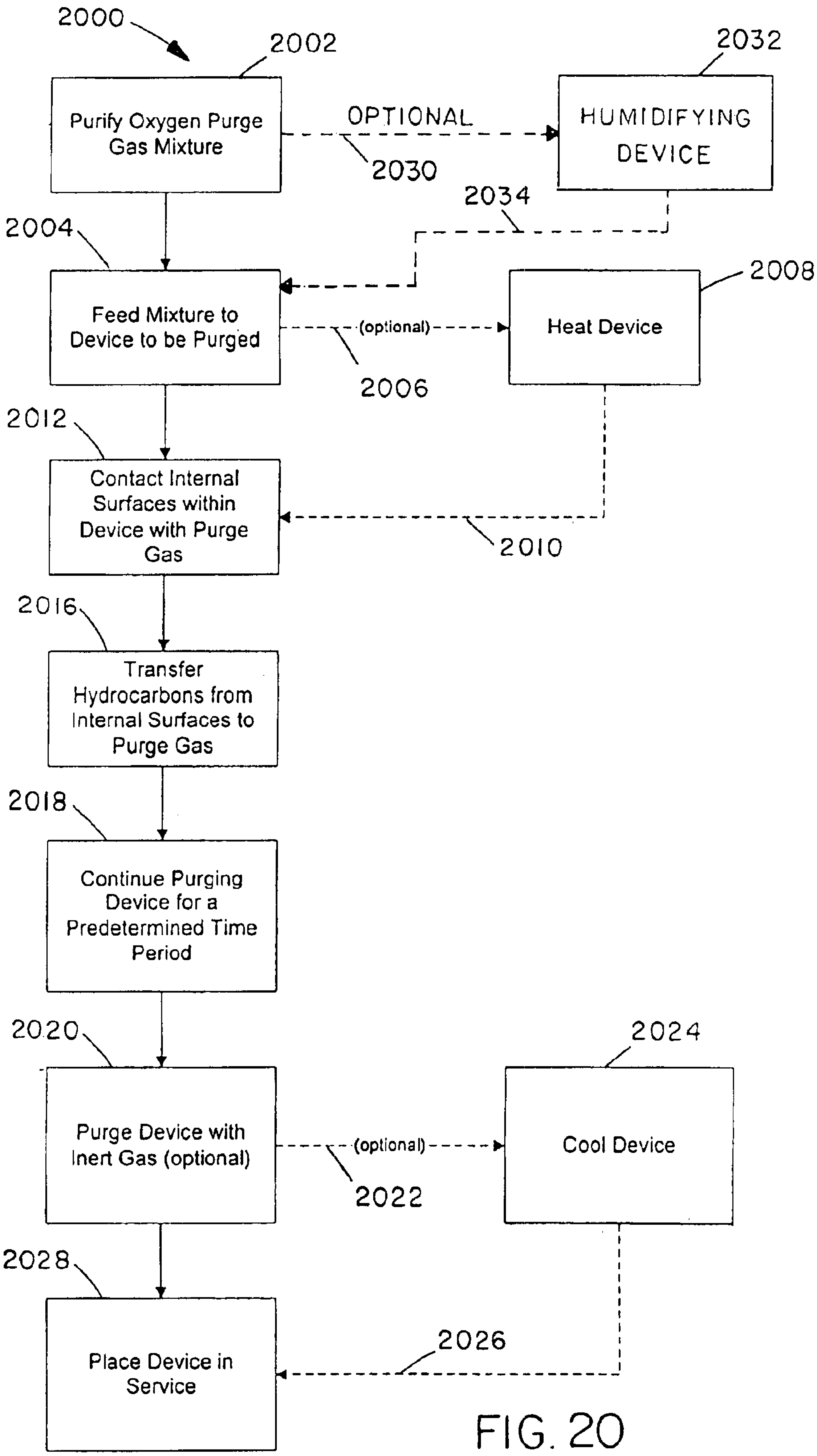
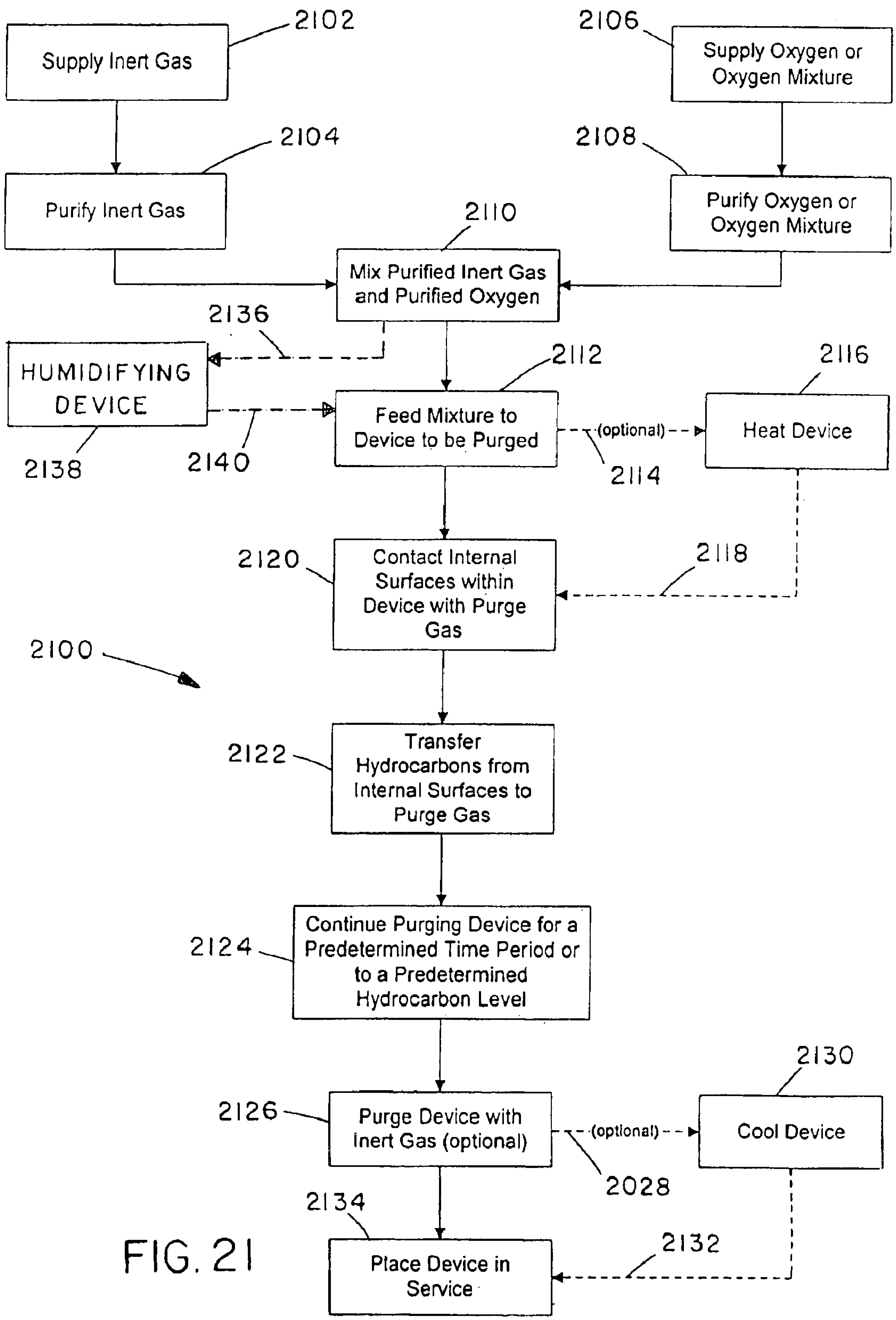

2000
2002
Purify Oxygen Purge Gas Mixture
OPTIONAL
2030
2032
HUMIDIFYING DEVICE
2034
2004
Feed Mixture to Device to be Purged
(optional)
2006
2008
Heat Device
2012
Contact Internal Surfaces within Device with Purge Gas
2010
2016
Transfer Hydrocarbons from Internal Surfaces to Purge Gas
2018
Continue Purging Device for a Predetermined Time Period
2020
Purge Device with Inert Gas (optional)
(optional)
2022
2024
Cool Device
2028
Place Device in Service
2026

FIG. 20



Supply Inert Gas
2102
2106
Supply Oxygen or Oxygen Mixture
Purify Inert Gas
2104
2108
Purify Oxygen or Oxygen Mixture
2110
Mix Purified Inert Gas and Purified Oxygen
2136
HUMIDIFYING DEVICE
2138
2140
2112
Feed Mixture to Device to be Purged
(optional)
2114
2116
Heat Device
2118
2120
Contact Internal Surfaces within Device with Purge Gas
2100
2122
Transfer Hydrocarbons from Internal Surfaces to Purge Gas
2124
Continue Purging Device for a Predetermined Time Period or to a Predetermined Hydrocarbon Level
2126
Purge Device with Inert Gas (optional)
(optional)
2028
2130
Cool Device
2134
Place Device in Service
2132

FIG. 21

METHOD FOR THE REMOVAL OF AIRBORNE MOLECULAR CONTAMINANTS USING WATER GAS MIXTURES

CROSS-REFERENCES TO RELATED APPLICATIONS

This application claims the benefit of priority of U.S. provisional application Ser. No. 60/475,145 filed Jun. 2, 2003 which is incorporated herein by reference in its entirety. This application is related to U.S. patent application Ser. No. 10/683,903 filed on Oct. 10, 2003 entitled "METHOD FOR THE REMOVAL OF AIRBORNE MOLECULAR CONTAMINANTS USING OXYGEN GAS MIXTURES."

FIELD OF THE INVENTION

The present invention generally relates to the purging of high purity components to remove contamination. More specifically, the present invention provides a method for removing airborne molecular contaminants from internal surfaces of high purity components and silicon substrates using purge gasses containing oxygen and/or water.

BACKGROUND OF THE INVENTION

In the manufacture of high purity products such as silicon wafers intended for semiconductor substrates or in the photolithography steps of manufacture of semiconductors, it is necessary to maintain a high degree of cleanliness. The products themselves must be clean, the atmospheres surrounding them throughout the manufacturing process must be clean, and the steps and equipment used in the manufacture must not impair cleanliness. It is well known that with the minute sizes of circuitry and components incorporated into semiconductor chips, even extremely small contaminant particles when deposited on chip surfaces are destructive of the chips. It is common for loss rates of wafers and chips during manufacturing due to system contamination to be a significant portion of the total production.

Manufacturers of wafers and chips have been engaged in extensive and continual efforts to improve on the cleanliness of their fabrication facilities ("fabs") including efforts to have manufacturing and process materials and gases be of high purity. Such efforts have been generally successful in the past, in that gases with purities defined by contaminant levels in the parts per million (ppm) and even into the parts per billion (ppb) ranges have been achieved. Generally improvements in process system cleanliness have paralleled increases in the component density of chips and reductions in the size of chip components and circuitry.

However, the ability of the prior art to achieve such parallel improvements in gases has more recently been severely taxed as the size of chip components has continued to decrease and component density has continued to increase. With the movement to 198 nm and 157 nm semiconductor technologies the ability of the products to tolerate contamination has substantially decreased, and process gases which previously were of adequate purities are no longer suitable. Scale-up techniques which previously achieved adequate improvements in the purity of such gases have been found to be ineffective in these "ultra high purity" (UHP) systems in which the lower nm level technologies are produced. Further, at the lower levels materials which were previously considered minor contaminants have been found to act as major contaminants, and the prior art gases have been found to be ineffective in removing such contaminant materials.

Ultrahigh purity products and process tools are susceptible to airborne molecular contaminants (AMCs) that can reduce product quality and yield. AMCs include, but are not limited to SO_x, NO_x, siloxanes, organophosphates, ammonia, moisture, oxygen and hydrocarbons (>4 carbons).

In the production of wafers for the semiconductor industry, there are three major sources of contamination, wafer storage containers (also known as foups) themselves; clean room air that enters the container as the wafers are moved between tools and the wafers themselves that may leech contaminants during the manufacturing and photolithography process. Methods have been developed to sufficiently reduce water and oxygen contamination in the manufacturing process. Additionally, methods have been developed for the removal of reaction products of the wafer with water and oxygen (e.g. silicon oxides) that can form on the surface of the wafers. However, technologies have not developed for the efficient removal of a number of airborne contaminants and their resulting reaction products on wafers.

Various contaminants have different effects. For example, in photolithography simple hydrocarbons that can condense on the lens assembly and result in transmission loss. Heavy hydrocarbons and significant concentrations of light hydrocarbons irreversibly deposit on optical surfaces and become graphitized by ultraviolet (UV) exposure. In a similar manner, Si containing organics, e.g. siloxanes, react under UV irradiation to produce SiO_2 crystallites that refract and absorb the incident light. Other AMCs, e.g. NO_x and SO_x, typically wherein $0<x\leqq 3$, cause optical hazing. Basic AMCs, e.g. amines, quench the photoacids, in addition to causing optical hazing. In the context of photolithography, oxygen and water can be deteremental to the production process and are typically to be considered AMCs. Recently, its has been reported by Veillerot et al. (Solid State Phenomena Vol. 92, 2003, pp 105–108) that atmospheric hydrocarbon contamination has a detrimental impact on 4.5 nm gate oxide integrity.

Approaches being tried to reduce this contamination include large-scale chemical filtration of the cleanroom air, moving from open to closed cassettes, and nitrogen purging of wafers during storage and transport. Nitrogen purging of UHP (Ultra High Purity) components such as valves and gas delivery piping, has been practiced for many years, and can be effective in removing oxygen and water. However, large scale use of nitrogen for purging large volume IC process equipment and large numbers of cassettes can be expensive and present a serious asphyxiation hazard. Additionally, it is suspected that nitrogen purging of hydrocarbon contaminated surfaces is not completely effective in removing the hydrocarbons.

Methods for analysis of contaminants in gas streams are well known. FIG. **1** (Prior Art) is a schematic flow diagram of a double dilution system **100** coupled to a gas chromatograph gas analysis system **120**. The double dilution system **100** comprising mass flow controllers **106**, **108**, **110**, and **112** enable the precise dilution of a gas standard **114** with a carrier gas **102** over a range of six orders of magnitude (10^6). Commonly available gas standards in the part per million (ppm) range can be effectively diluted to the part per trillion (ppt) range with system **100**. The dilution system **100** can be coupled to a gas chromatograph system **120** for the purposes of calibrating the response of the chromatograph **126**, by connecting the output **116** of the dilution system to the input **122** of the chromatographic gas analysis system **120**. A cold trap **124** accumulates condensed hydrocarbons in the sample, prior to injection into the gas chromatograph **126**. In this manner, the effective sensitivity of the chromatograph can be increased and ppt level hydrocarbon concentrations reliably measured.

FIG. **2** (Prior Art) is a calibration graph **200** of signal response area **204** versus sample hydrocarbon concentration **202** for various hydrocarbon molecules including benzene **206**, toluene **208**, ethyl-benzene **210**, meta, para-xylene **212**, ortho-xylene **214**, a second toluene **216**, for the analysis system **120** coupled to dilution system **100**. The data **220** show a linear response relationship between the peak area **204** and concentration **202** over almost six orders of magnitude, with a minimum sensitivity of 1 ppt.

FIG. **3** (Prior Art) is a graph **300** of time **302** versus gas chromatograph **126** detector signal **304** for a sample containing 1 ppt each of benzene, toluene, ethyl-benzene, and xylene. Here it can be seen that 1 ppt level concentrations for each of the hydrocarbons in the mixture result in clearly distinguished peaks for benzene **306**, toluene **308**, ethyl-benzene **310**, and xylene **312**.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for the removal of airborne molecular contaminants (AMCs) from surfaces within a device. In a first embodiment the method comprises the steps of introducing a purge gas containing oxygen and preferably having an AMC concentration of less than 1 part per billion on a volume basis into an interior portion of the device, contacting at least a portion of the surfaces with the purge gas, producing a contaminated purge gas by transferring a portion of the molecular contaminants from the surfaces into the purge gas, removing the contaminated purge gas from the device and, continuing the preceding steps until the contaminant concentration in the contaminated purge gas is decreased to a desired level, preferably below 1 part per billion on a volume basis. Additionally, the oxygen containing purge gas may further include moisture (i.e. water).

In a further embodiment of the present invention, the method comprises the steps of purifying a purge gas containing oxygen at a concentration between 1 and 25 volume %, also preferably having a molecular contaminant concentration of less than 1 ppb, introducing the purified purge gas into an interior portion of the device, contacting at least a portion of the surfaces with the purified purge gas, producing a contaminated purge gas by transferring a portion of the molecular contaminants from the surfaces into the purified purge gas, and removing the contaminated purge gas from said device. The method further comprises the step of continuing the preceding steps until a contaminant concentration in the contaminated purge gas is decreased to a desired level, preferably below 1 ppb. Additionally the oxygen containing purge gas may contain water at a concentration between about 100 ppm to about 2%.

In a third embodiment of the present invention, the method comprises the steps of purifying a purge gas containing water at a concentration between about 100 ppm and about 2% moisture with the overall mixture having a molecular contaminant concentration of less than 1 ppb, introducing the purified purge gas into an interior portion of the device, contacting at least a portion of the surfaces with the purified purge gas, producing a contaminated purge gas by transferring a portion of the molecular contaminants from the surfaces into the purified purge gas, and removing the purified purge gas from said device. The method further comprises the step of continuing the preceding steps until the contaminant concentration is the contaminated purge gas is decreased to a desired level, preferably below 100 ppt contaminant on a volume basis.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be better understood when consideration is given to the following detailed description thereof. Such description makes reference to the annexed drawings, wherein:

FIG. **1** (Prior Art) is a schematic flow diagram of a double dilution manifold coupled to a gas chromatograph gas analysis system;

FIG. **2** (Prior Art) is a calibration graph for the apparatus of FIG. **1** showing signal response area versus sample hydrocarbon concentration for various hydrocarbon molecules;

FIG. **3** (Prior Art) is a graph of gas chromatograph detector signal versus time for a sample containing 1 ppt each of various hydrocarbon components;

FIG. **4** is a schematic flow diagram of a testing setup according to an embodiment of the present invention;

FIG. **5** is a cross section schematic view of a wafer chamber according to an embodiment of the present invention;

FIG. **6** is a graph of hydrocarbon concentration versus time for two purge gas mixtures exiting the wafer chamber of FIG. **5**, with no wafer in the chamber, according to an embodiment of the present invention;

FIG. **7** is a graph of hydrocarbon concentration versus time for two purge gas mixtures exiting the wafer chamber of FIG. **5**, with a silicon wafer in the chamber, according to an embodiment of the present invention;

FIG. **8** is an expanded version of FIG. **7**, showing the time span from 10 hrs to 25 hrs in greater detail, according to an embodiment of the present invention;

FIG. **9** is a graph of m, p-xylene concentration versus time for three purge gas mixtures exiting the wafer chamber of FIG. **5**, with a silicon wafer in the chamber, the purge gasses containing 0%, 1%, and 20% oxygen, according to an embodiment of the present invention;

FIG. **10** is an expanded version of FIG. **9**, showing the time span from 5 hrs to 25 hrs in greater detail, according to an embodiment of the present invention;

FIG. **11** is a graph of hydrocarbon concentration versus time for five purge gas mixtures exiting the wafer chamber of FIG. **5**, with a silicon wafer in the chamber, the purge gasses containing 0%, 0.001%, 0.01%, 0.1%, and 1.0% oxygen, according to an embodiment of the present invention;

FIG. **12** is an expanded version of FIG. **11**, showing the time span from 10 hrs to 24 hrs in greater detail, according to an embodiment of the present invention;

FIG. **13** is a schematic flow diagram of the testing setup according to an embodiment of the invention.

FIG. **14** is a chromatograph of typical valve outgasing immediately after installation.

FIG. **15** is a chromatograph of typical valve outgassing at 80° C.

FIG. **16** is a graph of ethylbenzene concentration versus time for four purge gas mixtures exiting the wafer chamber of FIG. **5**, the purge gases containing 20% oxygen in nitrogen, 100% nitrogen, 0.5% water in nitrogen and 100 ppm water in nitrogen.

FIG. **17** is a graph of combined orthoxylene concentration versus time for four purge gas mixtures exiting the wafer chamber of FIG. **5**, the purge gases containing 20% oxygen in nitrogen, 100% nitrogen, 0.5% water in nitrogen and 100 ppm water in nitrogen.

FIG. **18** is a graph of p-xylene and m-xylene versus time for four purge gas mixtures exiting the wafer chamber of FIG. **5**, the purge gases containing 20% oxygen in nitrogen, 100% nitrogen, 0.5% water in nitrogen and 100 ppm water in nitrogen.

FIG. **19** is a process block diagram of a first purging process according to an embodiment of the present invention;

FIG. **20** is a process block diagram of a second purging process according to an embodiment of the present invention; and,

FIG. **21** is a process block diagram of a third purging process according to an embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The practice of purging UHP components and gas delivery systems in fabs has been common for many years. Purging and cleaning of equipment and substrates is also required in a number of other fields including, but not limited to, microelectronics, aerospace, optics for cleaning equipment such as LCD substrates, nanostructure surfaces, wafers, reticles and optical assemblies. Highly purified nitrogen and argon (less than 1 ppb oxygen, water vapor, CO, CO_2, and hydrocarbons) have generally been used as purge gases during the "dry down" of these components. The "dry down" process has been so named because the main purpose of the purging with nitrogen or argon was to remove adsorbed surface impurities such as water and oxygen.

Purge gases are typically inert. Removal of contaminants may occur by different mechanisms. During the purge process, contaminants diffuse into the purge gas and are carried away in the flow of the gas stream by reaching an equilibrium between the contaminant concentration in the purge gas and on the surfaces. This requires large volumes of UHP gases sufficiently clean to absorb contaminants at very low levels, typically ppb.

Contaminant species adsorbed onto silicon or stainless steel surfaces can also be desorbed by a kinetic effect. This takes place when a purge gas at high flow rate bombards the surface and collides with the adsorbed species. Kinetic energy may be transferred during the collision which can lead to desorption. In the above processes, there is nothing to prevent contaminants from readsorbing to the surfaces.

The present invention provides a potential new paradigm for the purging contaminants from silicon or stainless steel surfaces. It is proposed that in addition to kinetic energy, non-inert molecules such as oxygen and water, may exhibit a chemical effect. This is where oxygen or water, because of their electronegative and polarized nature respectively, has a strong affinity for the electropositive surface of the silicon or stainless steel and forms a weakly bound absorbed thin layer. Once a collision leads to desorption, re-adsorption of the contaminant species is hindered by the oxygen thin layer. In the case of water which forms stronger surface bonds, the thin layer is even more rigid and prevents readsorption. Since nitrogen is less electronegative than oxygen, the thin layer is very weakly bound and less effective. In addition, N_2 is lighter than O_2; therefore, it may have less of a kinetic effect. This proposed mechanism is not a limitation of the instant invention.

In the instant invention, the effective concentration of oxygen can vary over a wide range, as explained below. The nominal concentration of 17 to 21% oxygen, corresponding to that found in ordinary air, is inclusive in this effective concentration range, solving both the issue of cost and the asphyxiation hazard. Furthermore, these oxygen containing purge gas mixtures can be purified to a high degree, resulting in contaminant levels in the low ppt range. The purification processes known in the current art (generally for purifying oxygen) can be applied to the purification of clean dry air (CDA), a common reagent found in most industrial fab plants, or other oxygen mixtures. Purified air for use in the present invention (i.e. less than 100 ppt contaminants) will be referred to XCDA (extra clean dry air) to clearly distinguish it from CDA, a term commonly used in the art to refer to air with up to 100 ppm contaminant, typically 10–20 ppm contaminant. Purifiers for the preparation of XCDA are manufactured, for example, by Aeronex, Inc., of San Diego, Calif. Methods for preparation of oxygen and oxygen containing gases to sufficient levels of purity are well known to those skilled in the art (e.g. see U.S. Pat. No. 6,391,090, incorporated herein by reference).

The effective concentration of water in the purge gases of the instant invention may vary from about 100 ppm to about 2% in the apparatus to be purged, typically no more than 0.5%. Theoretically higher water concentrations can be used; however, such high concentrations can be impractical for removing from an apparatus before use. Of course, the lower cost and improved safety of the present invention would be of minimal use if the purging effectiveness could not be demonstrated. Since oxygen and water have been historically considered impurities, their use for removal of contaminants is unexpected. It shall be shown that not only are oxygen and/or water mixtures as effective as UHP nitrogen for removing hydrocarbons from surfaces, they actually show improved performance.

FIG. **4** is a schematic flow diagram of a testing setup according to an embodiment of the present invention. A double dilution system **100** as described previously is utilized to create known hydrocarbon concentrations from gas standard **114**. Concentration curves for other contaminants can be similarly established using methods well known to those skilled in the art. Nitrogen, XCDA, or other oxygen containing mixtures are fed to the carrier input **102**. When producing a hydrocarbon mixture to contaminate the surfaces of a test device, nitrogen is chosen at input **102**, the hydrocarbon component concentrations being determined by mass flow controllers **108–110** and the concentration of hydrocarbons in gas standard **114**. When the purging performance of the purge gas is being evaluated, either nitrogen or a mixture of nitrogen and oxygen are chosen at input **102**, with valve **109** closed and valves **107** and/or **111** open. Purifier **104** purifies the nitrogen or nitrogen oxygen mixtures. The gas mixtures created by system **100** are directed to the device under test (DUT) **402**. The hydrocarbon concentrations leaving the DUT **402** are introduced into the input **122** of the gas chromatograph gas analysis system **120**, where the hydrocarbon levels can be measured, as previously described and known to those skilled in the art.

Generally, the purging effectiveness of the oxygen mixtures was determined by first purging a test device with a hydrocarbon mixture in nitrogen to saturate the surfaces with hydrocarbons, then removing the hydrocarbons in the gas, and continuing the purging process with either UHP nitrogen or purified oxygen mixtures, measuring the hydrocarbon concentrations in the gas leaving the DUT. The faster the hydrocarbon concentration drops in the gas exiting the DUT, the more effective the purging process.

FIG. **5** is a cross section schematic view of a wafer chamber **500** according to an embodiment of the present invention. The wafer chamber is used to evaluate the effectiveness of purging hydrocarbons from stainless steel and silicon surfaces. The chamber has an inlet port **506**, an outlet port **508**, and supports **512** to hold 100 mm diameter silicon substrate **510** in the purge gas environment. The internal surfaces of the wafer chamber are electropolished 316 stainless steel. The wafer chamber diameter D (ref **502**) was 6.0 inches, having a height dimension H (ref **504**) of 3.9 inches. Wafer chamber **500** was connected as the DUT **402** in the system shown in FIG. **4**.

EXAMPLE 1

The effectiveness of removing hydrocarbons from 316 stainless steel electropolished surfaces with oxygen mixtures is demonstrated in this example. 316 stainless steel electropolished surfaces are widely used in UHP gas distribution systems in mass flow controllers, pressure regulators, and interconnecting pipe and tubing. They are also widely used as a process chamber material in semiconductor manufacturing equipment. An empty (no silicon wafer **510** present) wafer chamber **500**, was first purged with a nitrogen-hydrocarbon mixture containing approximately 10 ppb each of benzene, toluene, ethyl-benzene, meta/para-xylene, and ortho-xylene for approximately 3.5 hours. Following the hydrocarbon exposure, the wafer chamber was purged with UHP nitrogen and the hydrocarbon concentrations in the purge gas exiting the chamber were measured. The hydrocarbon exposure was then repeated. Following the second hydrocarbon exposure, the wafer chamber was purged with purified XCDA, which contained approximately 20% oxygen by volume.

FIG. **6** is a graph **600** of hydrocarbon concentration **604** versus time **602** for two purge gas mixtures exiting the wafer chamber of FIG. **5**, with no wafer in the chamber, according to an embodiment of the present invention. Broken curve **606** shows the total concentration decay response of all six hydrocarbons in the purge gas leaving the wafer chamber with a pure nitrogen purge gas. Solid curve **608** shows the total concentration decay response of all six hydrocarbons in the purge gas leaving the wafer chamber with a purified XCDA purge gas. Ref **610** indicates the point where the hydrocarbon containing purge gas was substituted for the nitrogen or XCDA. As can be seen from the relative position of the two curves **606** and **608**, the XCDA is more effective at removing the hydrocarbons contaminating the stainless steel surfaces of the wafer chamber, since the purge times to reach a given final hydrocarbon concentration are shorter with the XCDA.

The elution times of the hydrocarbons in curves **606** and **608** were compared to the time it would take to dilute the original 60 ppb hydrocarbon concentration to 10 ppt, given the wafer chamber volume of approximately 1.5 liters and purge flow rate of 0.75 liters/min. For a uniformly mixed system, it would take about 8.7 time constants to reduce an initial 60 ppb concentration to 10 ppt. The time constant is defined as the wafer chamber volume divided by the purge flow rate. At a time constant of approximately two minutes, simple dilution would take under 20 minutes to reach 10 ppt from an initial starting point of 60 ppb. The actual time for either the CDA or pure nitrogen to reach 10 ppt is considerably longer, indicating that removal from the internal stainless steel surfaces is dominating the hydrocarbon elution from the wafer chamber. Other tests have shown that once the hydrocarbons are reduced to very low levels (10 ppt and below) by purified XCDA, subsequent purging by UHP nitrogen does not produce hydrocarbon concentrations above the levels last obtained with the XCDA.

EXAMPLE 2

In this example, the test described in Example 1 was repeated, with the exception that a bare 100 mm (4 inch) silicon substrate **510** was placed in the wafer chamber **500** prior to exposure to the nitrogen-hydrocarbon mixture. FIG. **7** is a graph **700** of total hydrocarbon concentration **704** versus time **702** for two purge gas mixtures exiting the wafer chamber of FIG. **5**, with a silicon wafer in the chamber, according to an embodiment of the present invention. Curve **706** shows the decay in hydrocarbon concentration while the wafer chamber and wafer are purged with UHP nitrogen. Curve **708** shows the decay in hydrocarbon concentration while the wafer chamber and wafer are purged with purified XCDA. Ref **710** indicates the approximate point where feed of nitrogen-hydrocarbon mixture was terminated. Curves **706** and **708** clearly indicate hydrocarbon removal from silicon substrates is significantly slower than the stainless steel surfaces of the wafer chamber. As in the previous Example 1, the oxygen containing purge gas (curve **708**) shows a more rapid reduction in hydrocarbon concentration, when compared to UHP nitrogen (curve **706**). FIG. **8** is an expanded version of FIG. **7**, showing the time span from 10 hrs to 25 hrs in greater detail. Here it can be more clearly seen from graph **800** that hydrocarbon concentration **804** versus time **802** for the XCDA purge (curve **808**) is in advance of the UHP nitrogen curve **806**. At the 20 ppt concentration level, the UHP nitrogen response lags the XCDA response by nearly 5 hours. This, of course, means that it would require 5 hours longer to purge the wafer chamber and wafer to the 20 ppt level with UHP nitrogen.

EXAMPLE 3

FIG. **9** is a graph **900** of m, p-xylene concentration **904** versus time **902** for three purge gas mixtures exiting the wafer chamber of FIG. **5**, with a silicon wafer in the chamber, the purge gasses containing 0%, 1%, and 20% oxygen, according to an embodiment of the present invention. In this example, 1% oxygen and 20% oxygen (in nitrogen) are compared to UHP nitrogen. The hydrocarbon mixture used was approximately 10 ppb of meta-xylene and 10 ppb of para-xylene in nitrogen. As in Example 2, a silicon substrate was placed in the wafer chamber prior to the hydrocarbon exposure. Curve **906** in FIG. **9** shows the concentration response of both xylenes as a function of time during a UHP nitrogen purge. Curve **908** shows the concentration response of both xylenes as a function of time during a 1% oxygen (by volume) in nitrogen purge. Curve **910** shows the concentration response of both xylenes as a function of time during a 20% oxygen (by volume) in nitrogen (XCDA) purge. Ref **912** indicates the point at which the hydrocarbon feed gas was terminated. FIG. **10** is an expanded version of FIG. **9**, showing the time span from 5 hrs to 25 hrs in greater detail. Here it can be more clearly seen from graph **1000** that hydrocarbon concentration **1004** versus time **1002** for the 1% oxygen purge gas (curve **1008**) and the 20% oxygen purge gas (curve **1010**) is in advance of the UHP nitrogen curve **1006**. From a comparison of the three curves **1006–1010**, it can be noted that 1% oxygen is as effective as 20% for hydrocarbon levels above 10 ppt, but that the higher oxygen concentration has a slight advantage at levels below 10 ppt. Both oxygen containing purge gasses demonstrate a significant advantage over purging with UHP nitrogen.

EXAMPLE 4

FIG. **11** is a graph **1100** of hydrocarbon concentration **1104** versus time **1102** for five purge gas mixtures exiting the wafer chamber of FIG. **5**, with a silicon wafer in the chamber, the purge gasses containing 0%, 0.0001%, 0.01%, 0.1%, and 1.0% oxygen, according to an embodiment of the present invention. The hydrocarbon-nitrogen contamination mixture was 60 ppb total hydrocarbon concentration, as described in Example 1. Data representing the purge response of UHP nitrogen (ref **1106**, curve **1116**), 0.0001% oxygen (by volume) in nitrogen **1108**, 0.01% oxygen (by volume) in nitrogen **1110**, 0.1% oxygen (by volume) in nitrogen **1112**, and 1% oxygen (by volume) in nitrogen (ref **1114**, curve **1118**) are plotted in graph **1100**. All the data fall between the 0% oxygen curve **1116** (UHP nitrogen) and the 1% oxygen curve **1118**, as might be expected. Purging effectiveness increases as oxygen concentration increases within the ranges of oxygen concentration shown. FIG. **12** is an expanded version of FIG. **11**, showing the time span from 10 hrs to 24 hrs in greater detail. The graph **1200** of hydrocarbon concentration **1204** versus time **1202** is plotted with data representing the purge response of UHP nitrogen (ref **1206**, curve **1216**), 0.0001% oxygen **1208**, 0.01% oxygen **1210**, 0.1% oxygen **1212**, and 1% (ref **1214**, curve **1218**).

EXAMPLE 5

In a comparative test to determine the efficacy of XCDA as compared to nitrogen for decontamination of UHP equipment, a quantitative measurement system was assembled incorporating three commercial UHP diaphragm valves, each from a different manufacturer. The setup is shown in FIG. **13**, **1300**. To perform outgassing tests, each valve under test **1302**, VUT, was connected directly upstream of the cold trap **1304** as shown. Purified sample gas (N_2 or XCDA) was sent through each VUT with a gas purity specification of less than 1 ppt hydrocarbon. The supply N_2 and XCDA were purified with an inert purifier (Aeronex, SS-500KF-I-4R) and optics purifier (Aeronex, SS-700KF-O-4R) respectively. A heater tape and temperature probe were wrapped around the VUT to heat and monitor the temperature (not shown). As the gas purged through the VUT, any desorbed contaminants were collected downstream in the cold trap for hydrocarbon analysis in the gas chromatogram **1304**.

Valves were selected as representative of UHP system contamination sources since prior investigations had shown evidence of hydrocarbon contamination being generated by outgassing from elastomeric components in the valves. Detection and measurement was by means of cold trap collection and gas chromatographic measurement. The size of the contaminants was determined by retention time on the column (TOC) as compared to known standards. Chromatographs **1400** and **1500** showing time in minutes **1402** and **1502** versus mVolts **1404** and **1504**, respectively from the outgassing of valves at two different temperatures, ambient and about 80° C., are shown in FIGS. **14** and **15**. A rough analysis of the size of the contaminants based on the chromatographs is presented in Table 1 below.

TABLE 1

Analysis of contaminants by TOC

Time	Compound	% outgassing
<10 min	<5 carbons	10–20%
10–16 min	6–10 carbons	0–5%
16–25 min	11–15 carbons	20–40%
>25 min	>15 carbons	50–80%

It should be noted that the majority of the contaminants released are high molecular weight contaminants. This is in contrast to the prior examples where purging of low molecular weight hydrocarbons (i.e. less than 8 carbons) was analyzed.

Measurements were made at 0 and 60 minutes of system operation at ambient temperature (approximately 20° C.) and at 0, 60 and 720 minutes at 80° C. Measurements were made of both one-pass and two-pass purges by the different gases. In each case a nitrogen purge was followed by an XCDA purge. In the two-pass test the XCDA purge was followed by a second nitrogen purge. Tests of the three different UHP valves produced three different results. One valve started out with a low level on hydrocarbon outgassing and did not exceed 100 ppt even during elevated thermal XCDA testing, while another produced temperature sensitive contamination results. The remaining valve started out at 100 and peaked at 1000 ppt. On the positive side all valves through proper purging and thermal cycling where able to achieve levels at or below the 1 ppt lower limit of the detection capability of our test instruments. This indicates that through proper preconditioning any of these valves could be used in UHP piping system to deliver 1 ppt gas to the process. Results for the valve producing the 100–1000 ppt outgassing were as shown below in Table 2.

TABLE 2

Nitrogen vs. XCDA Purging of UHP Valves

No. of Passes	Time (minutes)	Temperature (C.)	Nitrogen (ppt)		XCDA (ppt)
1	0	Ambient	100		50
1	60	Ambient	180		50
1	0	80	1000		40
1	60	80	700		100
1	720	80	12		0
			1st	2nd	
2 (N2)	0	Ambient	100	0	50
2 (N2)	60	Ambient	180	0	50
2 (N2)	0	80	1000	0	40
2 (N2)	60	80	700	0	100
2 (N2)	720	80	12	0	0

It will be evident from the data of Table 2 that over all of the temperature and time ranges, purges with nitrogen produced only limited and quite unacceptable reductions of the hydrocarbon contamination of the valve. The subsequent purge with the XCDA reduced the hydrocarbon contaminant level to much lower levels, bettering the nitrogen purge lower limit by factors of 225. Further the XCDA purges to the low levels occurred in very short times as compared to the time required for the nitrogen purges to effect significant reductions. (The increases seen for the first nitrogen purge at ambient temperature and the XCDA purge at 80° C. between 0 and 60 minutes are believed to be due to the time required for some hydrocarbon contaminants within the elastomeric components to migrate to the surface for purging. This is a physical phenomenon of the elastomeric materials of the valve and not of the purge capabilities of the respective gases.)

The generally accepted protocol for UHP gas line validation requires extensive purging with nitrogen followed by verification that the line is contaminant free in a nitrogen purge environment. However, with all the valves XCDA volatilized additional hydrocarbons which remain after UHP nitrogen cleaning and thermal cycling. Even at ambient temperature, additional hydrocarbons were released when exposed to an oxygen rich purge gas.

A second series of tests were conducted to determine any effect from the order in which the purge gases were used.

Two equivalent commercial valves from the same manufacturer were tested for hydrocarbon decontamination. One (A1) was purged with nitrogen followed by XCDA, and the other (A2) with XCDA followed by nitrogen. The results are presented in Table 3 below,

TABLE 3

Nitrogen/XCDA Purge vs. XCDA/Nitrogen Purge

Time	Temperature	Valve A1		Valve A2	
		N2	XCDA		
(minutes)	(° C.)	(ppt)	(ppt)	XCDA (ppt)	N2 (ppt)
0	ambient	50	50	50	90
60	ambient	10	190	19	9
0	80	220	220	510	2
60	80	200	100	35	2
720	80	10	5	0	0

The XCDA step at ambient temperature produced results similar to the nitrogen purge. However, when Valve A2 was heated to 80° C. under XCDA purge, the hydrocarbon outgassing rate increased; significantly and then dropped quickly to below the limits of the detection equipment. Repeating the test in nitrogen showed little improvement. When purging with nitrogen, UHP components produced a continuous release of hydrocarbons. Actual peak values often did not occur until long after the initiation of purging due to the slow migration of heavier hydrocarbons through the piping system.

EXAMPLE 6

The effectiveness of removing hydrocarbons from 316 stainless steel electropolished surfaces with water mixtures is demonstrated in this example using a method similar to that in Example 1. Initially purified nitrogen gas was mixed with six components hydrocarbon gas standard (benzene, toluene, ethylbenzene, xylenes; BTEX) to create a known challenge of 60 ppb total organic compounds (TOC). The wafer chamber was purged with the challenge gas under standard operating conditions of 0.75 slm, 30 psig and ambient temperature. The wafer chamber effluent was measured for hydrocarbon level using a gas chromatograph with a flame ionization detector until its concentration reached 60 ppb±2 ppb hydrocarbon. The stabilization time for the chamber to condition occurred after 4–5 hours.

After the wafer chamber was saturated with the 60 ppb TOC, the BTEX challenge was turned off and moisture or oxygen was added to the nitrogen gas stream as indicated. The wafer chamber effluent was monitored until its TOC concentration dried down below the 10 ppt level for each contaminant.

FIG. **16** is a graph **1600** of time **1602** versus ethylbenzene concentration **1604** for four purge gas mixtures exiting the wafer chamber of FIG. **5**, the purge gasses containing 100% nitrogen, 20% oxygen, 0.5% water and 100 ppm water according to an embodiment of the present invention. The hydrocarbon-nitrogen contamination mixture was 60 ppb total hydrocarbon concentration, as described in Example 6. Data representing the purge response of ethylbenzene to UHP nitrogen **1608**, 20% oxygen (by volume) in nitrogen **1606**, 100 ppm water (by volume) in nitrogen **1610** and 0.5% water (by volume) in nitrogen **1612** are plotted in graph **1600**. Purging effectiveness increases as water concentration increases within the ranges of water concentration shown.

FIG. **17** is a graph **1700** of time **1702** versus o-xylene concentration **1704** for four purge gas mixtures exiting the wafer chamber of FIG. **5**, the purge gasses containing 100% nitrogen, 20% oxygen, 0.5% water and 100 ppm water according to an embodiment of the present invention. The hydrocarbon-nitrogen contamination mixture was 60 ppb total hydrocarbon concentration, as described in Example 6. Data representing the purge response of o-xylene to UHP nitrogen **1706**, 20% oxygen (by volume) in nitrogen **1708**, 100 ppm water (by volume) in nitrogen **1710** and 0.5% water (by volume) in nitrogen **1712** are plotted in graph **1700**. Purging effectiveness increases as water concentration increases within the ranges of water concentration shown.

FIG. **18** is a graph **1800** of time **1802** versus p- and m-xylene **1804** for four purge gas mixtures exiting the wafer chamber of FIG. **5**, the purge gasses containing 100% nitrogen, 20% oxygen, 0.5% water and 100 ppm water according to an embodiment of the present invention. The hydrocarbon-nitrogen contamination mixture was 60 ppb total hydrocarbon concentration, as described in Example 6. Data representing the purge response of p- and m-xylene to UHP nitrogen **1806**, 20% oxygen (by volume) in nitrogen **1808**, 100 ppm water (by volume) in nitrogen **1810** and 0.5% water (by volume) in nitrogen **1812** are plotted in graph **1600**. Purging effectiveness increases as water concentration increases within the ranges of water concentration shown.

FIG. **19** is a process block diagram **1900** of a first purging process according to an embodiment of the present invention. The process begins with step **1902**, wherein a purge gas mixture containing oxygen is purified. Moisture, when added, is typically added to the oxygen containing gas mixture after purification with step **1928** by passage through a humidifying device **1930**. Moisture may be added by any method known to those skilled in the art (e.g. a bubbler). However, methods that allow careful control of the amount of moisture added are preferred. A number of types of calibrated tubing with defined water permeabilities are known to those skilled in the art and are commercially available. Tubes are made of nylon, silicon, Teflon® (poly (ethylene tetraflouride); PTFE) and Nafion® (Dupont). The purified purge gas is passed through a chamber through which the tubing containing ultrapure water (less than 1 ppb contaminants) runs. The amount of moisture entering the purified purge gas can be determined for a specific flow rate of both water and purge gas. Such methods are well known to those skilled in the art. The humidified purge gas is delivered to the device in step **1932**.

The purified gas mixture is comprised of oxygen in a concentration between 99 volume % and 0.0001 volume %, preferably between 25 volume % and 0.1 volume %, and more preferably between 21 volume % and 1.0 volume %. Additionally, the purge gas contains water vapor at 100 ppm to 2%, preferably 100 ppm to 0.5%. The remainder of the mixture should be an inert gas chosen from among the group of nitrogen, the noble gasses, carbon dioxide, and methane. Preferably, nitrogen should be the major inert component, with all other components of the inert gas being present at below about 1 volume %. Preferably, the levels of non-methane hydrocarbons, volatile bases, volatile acids, refractory compounds, and volatile metal compounds should be below 1 ppb. Preferably, the levels of contaminants should be below 100 ppt, more preferably below 10 ppt, most preferably below 1 ppt. The specific purification means is well known to those skilled in the art.

In step **1904**, the purified purge gas containing oxygen and/or water is fed to the device to be purged. Optionally, the device may be heated in step **1908** to reduce the purge time. If heating is employed, the process proceeds along paths **1906** and **1910** to step **1912**. In step **1912**, a portion of the internal surfaces are contacted with the oxygen and/or water containing purge gas. In step **1914**, a portion of the contaminants present on the internal surfaces of the device are transferred to the purge gas, creating a contaminated purge gas. Surfaces contained within the device being purged may be metal, metal oxides, silicon, silicon oxides, ceramics, or plastics. Preferably, the surfaces are electropolished stainless steel, silicon, and oxides of silicon. Also in step **1914**, the contaminated purge gas is removed from the device. In step **1916**, the purging process is continued until the contaminant concentration in the purge gas is below a predetermined limit. This limit may be less than 1 ppb, preferably less than 100 ppt, more preferably less than 10 ppt, most preferably less than 1 ppt. In a preferred optional step **1918**, the oxygen and water containing purge gas may be removed by purging with a dry gas including oxygen, nitrogen or other inert gas to remove the water which is incompatible with a number of high purity applications. In optional step **1918**, the oxygen containing purge gas may be removed by purging with nitrogen or another inert gas, if the device is to be placed into service where oxygen may be considered undesirable. If the device was heated, the device should be cooled in step **1922** and returned to service in step **1926** via paths **1920** and **1924**.

FIG. **20** is a process block diagram **2000** of a second purging process according to an embodiment of the present invention. The process begins with step **2002**, wherein a purge gas mixture containing oxygen is purified. The requirements for the inert gas are as described above. Purification means to obtain such high purity gases are well known to those skilled in the art. In step **2004**, the purified purge gas containing oxygen is optionally fed, in step **2030**, to a humidifying device **2032** and returned in step **2034** to be fed to the device to be purged. Optionally, the device may be heated in step **2008** to reduce the purge time. If heating is employed, the process proceeds along paths **2006** and **2010** to step **2012**. In step **2012**, a portion of the internal surfaces are contacted with the oxygen and/or water containing purge gas. In step **2016**, a portion of the contaminants present on the internal surfaces of the device are transferred to the purge gas, creating a contaminated purge gas. Surfaces contained within the device being purged may be metal, metal oxides, silicon, silicon oxides, ceramics, or plastics. Preferably, the surfaces are electropolished stainless steel, silicon, and oxides of silicon. Also in step **2016**, the contaminated purge gas is removed from the device. In step **2018**, the purging process is continued for a predetermined time period. This may be more convenient than basing the purge time on the measurement of contaminant concentration, which requires complex and sensitive analytical equipment. In a preferred optional step **2020**, the oxygen and water containing purge gas may be removed by purging with a dry gas including oxygen, nitrogen or other inert gas to remove the water which is incompatible with a number of high purity applications. If the device is to be placed into service where oxygen may be considered undesirable, nitrogen or inert gas should be used for the post-cleaning purge. If the device was heated, the device should be cooled in step **2024** and returned to service in step **2028** via paths **2022** and **2026**.

FIG. **21** is a process block diagram **2100** of a third purging process according to an embodiment of the present invention. In step **2102**, an inert gas is supplied. The requirements for the inert gas are as described above. In step **2104**, the inert gas is purified via a process or processes well known to those skilled in the art. In step **2106**, essentially pure oxygen or a mixture containing oxygen is supplied. In step **2108**, the oxygen or oxygen mixture is purified as well known to those skilled in the art. In step **2110**, the purified oxygen or oxygen mixture from step **2108** is combined with the purified inert gas from step **2104**. Optionally, the purification stages may be performed after the combining of the gasses in step **2110**. After step **2110**, the purified purge gas containing oxygen is optionally fed, in step **2136**, to a humidifying device **2138** and returned in step **2140**, so that the purified purge gas containing oxygen and/or water is fed to the device to be purged. Optionally, the device may be heated in step **2116** to reduce the purge time. If heating is employed, the process proceeds along paths **2114** and **2118** to step **2120**. In step **2120**, a portion of the internal surfaces are contacted with the oxygen containing purge gas. In step **2122**, a portion of the hydrocarbons contaminating the internal surfaces of the device are transferred to the purge gas, creating a hydrocarbon contaminated purge gas. Surfaces contained within the device being purged may be metal, metal oxides, silicon, silicon oxides, ceramics, or plastics. Preferably, the surfaces are electropolished stainless steel, silicon, and oxides of silicon. Also in step **2122**, the hydrocarbon purge gas is removed from the device. In step **2124**, the purging process is continued for a predetermined time period, or to a predetermined hydrocarbon level. This level may be less than 100 ppt, but is preferably less than 10 ppt. In a preferred optional step **2126**, the oxygen and water containing purge gas may be removed by purging with a dry gas including oxygen, nitrogen or other inert gas to remove the water which is incompatible with a number of high purity applications. If the device is to be placed into service where oxygen may be considered undesirable, nitrogen or inert gas should be used for the post-cleaning purge. If the device was heated, the device should be cooled in step **2130** and returned to service in step **2134** via paths **2128** and **2132**.

What is claimed is:

1. A method for the removal of airborne molecular contaminants (AMC) from a substrate comprising the steps of:

providing a purified purge gas, wherein the purified purge gas comprises water at a concentration of at least about 100 parts per million (ppm) on a volume basis, the purified purge gas having an AMC concentration less than about 1 part per billion (ppb) on a volume basis;

contacting at least a portion of the substrate with the purified purge gas;

producing a contaminated purge gas by transferring AMC from the substrate into the purified purge gas; and

removing the contaminated purge gas from the substrate;

thereby removing AMC from the substrate.

2. The method as in claim **1**, wherein the steps are repeated until the contaminated purge gas has an AMC concentration below about 100 parts per trillion (ppt) on a volume basis.

3. The method as in claim **1**, wherein the AMC concentration of the purified purge gas is less than about 10 ppt AMC on a volume basis.

4. The method as in claim **1**, wherein the AMC concentration of the purified purge gas is less than about 1 ppt AMC on a volume basis.

5. The method as in claim **1**, wherein the water comprises 100 ppm to 2% by volume.

6. The method as in claim **1** further comprising purging of the substrate with an inert gas after removing said contaminated purge gas from said substrate.

7. The method as in claim **1**, wherein the substrate is enclosed within a chamber.

8. The method as in claim **1**, wherein said contacting of said substrate with said purified purge gas removes said AMC from said substrate at a faster rate than using a nitrogen purge gas.

9. The method as in claim **6**, wherein said inert gas is selected from the group consisting of nitrogen, argon, noble gases and methane.

10. The method as in claim **7**, wherein the substrate includes at least one silicon substrate.

11. The method as in claim **7**, wherein the substrate includes a wafer.

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